# POLYESTERS, THERMOPLASTIC

## 1. Introduction

Thermoplastic polyesters enter into an extraordinary variety of everyday products: fibers, textiles, tire-cord, safety belts, ropes, lifting slings, consumer goods, medical accessories, automotive parts, electronic items, photographic film, magnetic tape, film base for audio and video recording, packaging materials, bottles, and containers to list only a few. This broad span of applications illustrates the wide utility of such materials. This article considers nonfiber applications of polyesters. It begins by describing the properties, synthesis, manufacture, and raw materials for these polyesters. Specific polymers, their fabrication, applications, and relevant commercial information will be considered. In order to keep the article to a manageable length, it is confined to semicrystalline thermoplastic polyesters. It does not consider unsaturated polyester thermosets, polyester films, nor thermoformed sheets, all of which are described elsewhere (article). Blow-molded polyester containers are dealt with in some detail, because this is a very large volume market that has expanded enormously over the last 15 years and is still growing.

The main polymers to be described are poly(ethylene terephthalate), PET, [25038-59-9]; poly(butyleneterephthalate), PBT, [26062-94-2]; poly(trimethylene terephthalate), PTT, [26546-03-2], poly(cyclohexanedimethyleneterephthalate), CHDMT, [24936-69-4], and poly(ethylenenaphthalene-2,6-dicarboxylate), PEN, [24968-11-4]. This article will also deal with high performance liquid crystalline all-aromatic polyesters, eg, VECTRA [70679-92-4, 82538-13-4] and XYDAR [31072-56-7] and ZENITE. Noncrystalline aromatic polycarbonates and polyesters (polyarylates) and alloys of polycarbonate with other thermoplastics will not be considered, neither are aliphatic polyesters derived from biological sources, such as poly(3-hydroxybutyrate), poly(glycolide), or poly(lactide) as these, too, are separately covered. Thermoplastic elastomers derived from polyesterether block copolymers such as PBT/PTMEG-T [82662-36-0] are included in the section on poly(butyleneterephthalate). Specific polymers will be considered roughly in order of volume, which puts PET first by virtue of its enormous market volume in bottle resin.

## 2. A Brief Historical Survey of Commercial Polyesters

The polyesters we are dealing with are *linear polymeric molecules containing in-chain ester groups*, formally derived from condensation of a diacid with a diol. The topic has been reviewed in depth by Goodman (1). While polymers containing ester bonds like cellulose acetate and glycerol/phthalic anhydride (glyptal) resins were developed as aircraft dopes, varnishes, and coatings during World War I (WWI), these are not polyesters as defined above. Only when Carothers began his classic work in the early 1930s were linear polyesters examined in a systematic fashion (2). In his pioneering research, Carothers studied a range of aliphatic polyesters, but did not pursue polyesters derived from *aromatic* diacids and aliphatic diols. All his polymers were of low melting point and were soluble in common organic dry cleaning solvents. They had little utility as practical textile fibers; hence his move to polyamides, which were insoluble in such solvents, and the eventual discovery of nylon.

The first successful synthesis of a satisfactory high molecular weight textile polyester was PET, which was made in the United Kingdom during the early days of World War II (WWII) by Whinfield and Dickson in 1942 while working at the Calico Printers' Association (3,4). The material was quickly recognized as a basis for a valuable melt-spinnable synthetic fiber, but no serious commercialization could be carried out until the end of the war. In the United Kingdom, fiber melt-spun from the new polyester was manufactured by Imperial Chemical Industries Ltd. under the trade name TERYLENE, while DuPont introduced it to the United States in 1953 under the trade name DACRON.

Work went on in both the United States and Europe, notably at DuPont and ICI Ltd. in the United Kingdom, on exploring the whole series of alkylene terephthalate polymers in connection with new synthetic fibers. Poly(1,4-butyleneterephthalate), 4GT, or PBT, was investigated in great detail because had attractive fiber properties. Notably, it was very white and resisted photooxidative yellowing much better than did nylon; it could be dyed with disperse dyes much more easily than PET and, above all, it had far better fiber resilience and elastic recovery properties than PET. These made it attractive for such fiber end-uses as women's wear, hosiery, and carpets. However, PBT fiber had two serious drawbacks: Because of its low $T_g$, it could not meet the twin criteria of pleat-retention and crease-resistance in apparel fabrics, which were commercially important in the mid-1950s (PET fibers were introduced just at a time when accordion pleated skirts were highly fashionable). Furthermore, PBT was relatively expensive, due to the high cost of butane-1,4-diol. Later it was realized that PBT polymer was not only highly crystalline, but had a high *rate of crystallization*, two qualities ideally suited to an injection molding resin. In comparison with nylon, it had a low moisture uptake and was much more dimensionally stable to changes in atmospheric humidity. Molding-grade PBT resins were introduced by Celanese Corp. in 1970.

In the mid-1950s, Eastman Kodak workers had been working on a new polymer to enter the polyester fiber market. To secure their own composition-of-matter claims, they devised a new diol, not previously disclosed in the original Whinfield patents. This was 1,4-cyclohexanedimethanol [105-08-5], a cyclic diol made by the exhaustive hydrogenation of dimethyl terephthalate. Reacting this new diol with dimethyl terephthalate gave a crystalline polyester with a higher melting point than PET and it was introduced in the United States in 1958 as a polyester staple fiber under the trade name Kodel (5). Much later, the same polyester, now called PCT, and a cyclohexanedimethanol–terephthalate–isophthalate copolymer were introduced as molding resins and thermoforming materials (6). More recently, copolymers of PET with CHDM units have been used for blow-molded bottle resins (7).

Notwithstanding its good physical properties and chemical stability, PET itself was not successful as an injection molding resin, due to its low crystallization rate in a cold mold. The mold had to be heated to 130–40°C, well above the $T_g$ of PET to obtain adequate crystallization and, even then, satisfactory moldings were not obtained due to the uncontrolled morphology. From the mid-1960s onward, fast-crystallizing grades of PET were developed that gave uniform and controlled morphology, due to the presence of nucleating agents (8–10). Both AKZO and Du Pont were early entrants into the field with their ARNITE and RYNITE range of PET resins; other manufacturers followed. PET molding resins are now widely used, particularly in the auto industry. However, the biggest single market for moldable PET nowadays is blow-molded bottles, which exceeds every other single end-use for PET polymer except fibers. In 1990, the annual world production of PET fibers was $\sim$ 9 million tons; the annual production of PET bottle resin in 1990 was 1.2 million tons. By 2005–2006 the total world PET polymer market is estimated to be slightly $>$ 40 million metric tons, of which approximately one-third (say 14 million metric tons) will be bottle resin. The rate of growth of bottle resin is far higher than that of PET fibers with explosive growth in China and the Far East (11).

In the late 1940s the superior properties of films and fibers (code-name Fiber-Q) made from poly(ethylene-2,6-naphthalenedicarboxylate), PEN, were recognized. This was first synthesized by ICI workers in 1948 (12). The polyester was not a commercial possibility until economical routes to naphthalene-2,6-dicarboxlic acid, NDA, [1141-38-4] were found. Two firms brought commercial plants on stream for the production of NDA and its dimethyl ester (DMNDA) $\sim$ 1996–1998. These were Amoco (later BP Chemicals) in the United States at Decatur, Alabama, and Mitsubishi Gas Chemical in Japan (13). Others have followed, notably in the Far East, such as Kobelco (Kobe Steel Ltd.). The PEN film for audio- and video-tape and blow-molded PEN containers for hot-fill applications are already being marketed in Japan and Europe. The NDA is unlikely ever to become as inexpensive as terephthalic acid, but its polyesters are being used increasingly where better heat resistance and physical properties are important. The PEN high strength polyester fibers are now marketed commercially by Honeywell under the trade name Pentex (see http://www.performance-fibers.com). Other NDA-based polyesters may become available if a market need exists. One example could be the experimental polyester called PBN; the NDA analogue of PBT, poly(1,4-butylenenaphthalene-2,6-dicarboxylate) [28779-82-0]. It has a very high rate of crystallization, faster even than that of PBT, and its combination of physical properties is well suited for injection molding (14).

Liquid-crystalline thermotropic polyesters were discovered independently in several places during the late 1960s and early 1970s. Notable are the work of Economy and Cottis at Carborundum Corporation (15–17), Jackson at Eastman (18,19), and Schaefgen and co-workers at Du Pont (20–23). They all made the crucial discovery that certain all-aromatic copolyesters derived either from aromatic hydroxy acids or by reaction of an aromatic diacid with an aromatic diol, could exist in a mesophase or liquid-crystal state well below their thermal decomposition temperature. In fact, work on all-aromatic high melting polyesters had been carried out 10 years earlier at ICI Fibres in Harrogate, the United Kingdom, during 1962–1963 by Goodman, McIntyre, Stimpson, and East, among others. Thermotropic behavior (birefringent melt) was actually observed in March 1963, but at this early date, its true significance was not appreciated (24). During the mid-1970s, while working on a melt-spun high modulus all-aromatic polyester fibers at Celanese Corporation's Robert L. Mitchell Technical Center in Summit, NJ, Calundann (25) discovered the unique properties of aromatic polyesters derived from 6-hydroxy-2-naphthoic acid, HNA [16712-64-4]. These polymers were liquid crystalline, yet had moderate melting points (ie, solid-nematic mesophase transition) in the region 240–300°C. They were easily processed into high performance fibers. Copolyesters derived from HNA and HBA, 4-hydroxybenzoic acid [99-96-7] became the basis of the VECTRA series of liquid-crystal polymers. Meanwhile, the original Carborundum work had led via licensing arrangements to commercialization of other high melting thermotropic polyesters, first by Sumitomo in Japan and later by Dart Corporation (later Amoco and now Solvay Polymers) in the United States under the trade name XYDAR. Du Pont (now Invista) entered the field somewhat later with their ZENITE range of LCPs based upon naphthalene-2,6-dicarboxylic acid.

Liquid-crystal polymers have a unique combination of high thermal stability, outstanding chemical and solvent resistance, very good melt–flow properties and low shrinkage, all ideally suited to the precision injection molding of complex shapes, such as those widely used in electronic components. During the last 15 years the business has seen steady growth, both in the United States and in the Far East. Somewhat ironically, now that the commercial success of LCP molded plastics is well established, commercial development of fibers and monofils (eg, VECTRAN) from the same materials is underway in Japan, some 20 years after the idea was originally envisaged!

## 3. Manufacture of Polyesters: Raw Materials and Monomers

Both PET and PBT are made from terephthalic acid and its dimethyl ester. Terephthalic acid is made by the air-oxidation of *p*-xylene [106-42-3] in acetic acid under moderate pressure in the presence of catalysts, such as divalent cobalt and manganese bromides (26). *p*-Xylene is the highest melting of the three isomeric dimethylbenzenes and is separated by fractional crystallization from the

C8 aromatic fraction, which includes ethylbenzene, during petroleum refining (27). Alternatively, it may be separated by selective adsorption on a zeolite bed combined with an isomerization process (28). The PET fiber production requires very pure tetraphthalic acid (TA). In the early days, the oxidation of *p*-xylene used 50% aqueous nitric acid under pressure, a process that left many very undesirable by-products (eg, nitro aromatics and carbazoles) in the crude product. Because of the extreme insolubility of TA, it was not a product easily purified so it was converted to its dimethyl ester (dimethyl terephthalate, DMT) and the DMT purified by distillation under reduced pressure and finally recrystallized. The PET polymer was made by reacting DMT with excess ethylene glycol in the presence of catalysts to promote ester interchange and polymerization (see later). During the late 1960s and early 1970s, pure TA became available in large quantities (29) due to improvements in the xylene oxidation process and the purification of crude TA. The most notable air-oxidation impurities were *p*-toluic acid and the very harmful (from a polymer viewpoint) 4-carboxybenzaldehyde (4-CBA). These impurities were eliminated by recrystallization from aqueous solution under high pressure with concomitant hydrogenation over a fixed-catalyst bed. Under these conditions, *p*-toluic acid is easily soluble in superheated water and any 4-CBA present is hydrogenated to toluic acid, thus removing it (30). The availability of pure TA caused major changes in the production of PET for fibers. The direct esterification (DE) process superseded the former ester interchange (EI) process based upon DMT. Interestingly, DMT has made a partial come back due to recycling waste PET (31,32). Distillation of DMT derived from the methanolysis/glycolysis of waste PET is now being carried out on a multimillion pound scale.

The industrial synthesis of naphthalene-2,6-dicarboxylic acid (NDA) is decidedly more complex than that of terephthalic acid because, unlike *p*-xylene, 2,6-dimethyl-naphthalene [581-42-0] is not so readily isolable from petroleum refining. The ring can be constructed by stepwise synthesis (33–35). In a typical scheme, toluene reacts with carbon monoxide and butene-1 under pressure in the presence of hydrogen fluoride and boron trifluoride to give 4-methyl-*sec*-butyrophenone, which is reduced to the corresponding carbinol and dehydrated to the olefin. The latter is cyclized and dehydrogenated over a special alumina-supported catalyst to give pure 2,6-dimethylnaphthalene, free from all isomers. It is also possible to reisomerize various mixed dimethylnaphthalenes to the 2,6-isomer in the presence of hydrogen fluoride (36). The 2,6-dimethylnaphthalene is air oxidized to NDA (37) under similar conditions to those used for terephthalic acid. There are many additional complications with NDA oxidation that present problems not found in the TA process. In any naphthalene structure, due to its quinonoid character, one aromatic ring is always liable to oxidative attack. Hence, by-products like trimellitic acid [528-44-9] are formed. Another harmful impurity is 6-formyl-2-naphthoic acid, analogous to 4-CBA in the TA process. Ring-brominated aromatic species derived from the inorganic bromides used as oxidation cocatalysts are also present as impurities. The crude NDA is converted to its dimethyl ester (DMNDA) [840-65-3] and solvent recrystallized to give a high purity diester (38–40). A process for purifying NDA directly by hydrogenation somewhat comparable to the pure TA process, has been described (41). Since 1995, some 78 U.S. patents have issued concerning PEN and NDA synthesis.

Several of these describe refinements to the NDA and dimethylnaphthalene (DMN) processes. A route due to Takagawa (42) for pure 2,6-DMN involves reaction of *o*-xylene with butadiene to give *o*-tolyl-2-pentene, which is cyclized and dehydrogenated to 1,5-dimethyl-naphthalene. This is isomerized over an alumina/mordenite catalyst to a mixture of DMN isomers, from which the desired 2,6-DMN can be isolated, since it has the highest melting point (112°C). A specific problem with this route is the presence of 2,7-DMN, which melts at 92°C, but has exactly the same boiling point as 2,6-DMN (262°C) so that a complex system of fractional distillation and subsequent fractional crystallization must be employed. Other new process patents describe improved oxidation reactions that minimize the production of trimellitic acid and the wasteful loss of cobalt and manganese salts used as oxidation catalysts (43). New oxidation catalysts containing copper salts with halides and metals like vanadium are widely adaptable (44). A recent patent describes a simple way to remove harmful aldehydes (4-CBA in TA and 6-formyl-2-naphthoic acid in NDA) by a controlled reoxidation of the aldehyde acids to dicarboxylic acids, instead of reducing them as in the Amoco process. The latter wastes valuable aromatic ring precursors, particularly in the NDA process (45).

Turning now to the diol components, ethylene glycol (ethane-1,2-diol) is made from ethylene by direct air oxidation to ethylene oxide and ring opening with water to give the 1,2-diol (46). Butane-1,4-diol is still made by the Reppe process dating back to pre-WWII Germany. Acetylene is reacted with formaldehyde in the presence of catalyst to give 2-butyne-1,4-diol, which is hydrogenated to butanediol. The ethynylation step depends on a special cuprous acetylide-bismuth salt catalyst that minimizes side reactions (47). The hydrogenation step is best done in two stages over special catalysts (48). Two alternative butanediol routes both start from butadiene. In the first process, due to Mitsubishi Chemical Industries, butadiene reacts with acetic acid and oxygen in the presence of a palladium catalyst to give 1,4-diacetoxy-but-2-ene (49) and the latter is hydrogenated over a special catalyst (50), and finally hydrolyzed to 1,4-butanediol. The other butanediol process relies on the hydroformylation of allyl alcohol (made from propylene oxide, from air oxidation of propene) over a rhodium catalyst (51) to give 4-hydroxybutyraldehyde. This is reduced to butanediol (52). The ethynylation route is still the most important one, but ARCO have commercialized a hydroformylation process. Butane-1,4-diol freezes at 20°C, hence its shipping and handling facilities need to be heat traced if the local climate demands it.

Cyclohexanedimethanol (53) starts from dimethyl terephthalate. The aromatic ring is hydrogenated in methanol over a palladium catalyst to dimethyl cyclohexane-1,4-dicarboxylate (hexahydro-DMT) and the ester groups are further reduced under very high pressure, using copper chromite catalysts, to the bis primary alcohol, usually as a 68:32 mixture of trans and cis forms. The mixed diol is a sticky low melting solid, mp 45–50°C. The pure cis diol melts at 43°C while the pure trans isomer melts at 67°C. A process for hydrogenating waste PET polymer in methanol directly to form cyclohexane-dimethanol has been described (54).

A new polyester resin was announced during 1995 (55) by Shell Chemical Co. and shortly afterward by Du Pont. This polymer is PTT, poly(trimethylene-terephthalate), sometimes called 3GT [26546-03-2], which is derived from terephthalic acid and propane-1,3-diol [504-63-2]. The chemistry of this polymer has been recently reviewed in detail by Chuah (56). This is another polyester originally invented by Whinfield and was recognized at an early stage for its outstanding fiber resilience. It was not commercially feasible until an economic synthesis of the diol was available. Although the molecule looks to be a simple one, commercial routes were a long time coming. Two main processes have now come on stream for the economic production of propane-1,3-diol (PDO). The first (57) uses hydroformylation of ethylene oxide to 3-hydroxypropanal and its subsequent reduction to PDO. The hydroxypropanal can also be made by hydration of acrolein in a process due to Degussa (58). There are numerous patents for new catalysts for the propanal-PDO reduction step. The current Shell process is believed to use a nickel–molybdenum catalyst (59). A modified Shell process uses methoxycarbonylation (carbon monoxide and methanol) of ethylene oxide to methyl 3-hydroxypropanoate, using cobalt octacarbonyl as a catalyst. The ester is hydrogenated to the diol over a copper–zinc oxide catalyst without isolation. This route gives a high product yield because it avoids the immiscible acetal and hemi-acetal impurities formed by self-condensation of 3-hydroxypropanal (60).

The DuPont process (61,62) is considerably more imaginative as it uses a fermentation process to make PDO from carbohydrate sources (corn sugar). This is truly a large scale application of green chemistry. It has long been known that glycerol can be made by a modified fermentation, dihydroxy-acetone being an intermediate. Such processes were used during WWI to make munitions. Du Pont have used genetic engineering in collaboration with Genencore International to produce new microorganisms (*Escherichia coli* containing genes from *Saccharomyces cerevisiae* and *Klebsiella pneumoniae*) that form PDO in place of glycerol in high yield and can also survive the high concentration of PDO in the fermentation liquor. A recent patent (63) claims a microorganism that will function at PDO broth concentration levels of 105 g/L. The diol is harvested by solvent extraction or by use of molecular sieves (64). In June 2003 DuPont were awarded a Presidential Green Chemistry Challenge Award for their PDO process (65). In 2004, Tale and Lyle PLC joined forces with Du Pont to form a new joint venture to make chemical intermediates from renewable resources. A new joint PDO plant is due for completion at Loudon, Tennessee, in March 2006 (66). The main commercial targets of the new polyester are apparel (sports and women's wear) and carpet fiber, both of which exploit the fiber's exceptional resilience and desirable fabric esthetics (67). As a molding resin, PTT crystallizes readily, almost as fast as PBT and it has a similar melting point and $T_g$ to PBT (56). Its crystal structure has been determined by two groups of workers (68,69). One source (70) suggests that the new processes may make propane-1,3-diol significantly cheaper than butane-1,4-diol and only slightly more expensive than ethylene glycol. Already glass-filled PTT molding resins are available (71).

Cyclohexyldimethanol terephthalate (CHDMT) has been reviewed in depth by Turner and co-workers (72). The polymer was orginally introduced by Eastman in 1958 as a polyester staple fiber under the name Kodel (5,73). Eastman later manufactured PET fiber under the brand name Kodel-II but abandoned the staple fiber business in 1993. They have since expanded their CHDMT business in molding resins and bottle resins. The cyclic diol exists in cis and trans forms: fortuitously, the two homopolymers are both crystalline and form copolymers with no minimum melting point composition. The melting points and $T_g$ values rise monotonically from the pure cis polymer ($T_m$ 251–256°C; $T_g$ 60°C) to the pure *trans* polymer ($T_m$ 312–318°C; $T_g$ 90–95°C) a situation that is decidedly unusual (74). The usual 70:30 glycol mixture gives a polymer melt temperature ∼290°C. Because the $T_g$ of CHDMT is higher than that of PET, the temperature of maximum crystallization rate is higher.

The PEN polymers have been comprehensively reviewed recently by Sakellarides (75).The polymerization route is somewhat similar to that of PET and the starting material is almost always the dimethyl ester of NDA (DMNDA) as previously explained. The melting point of PEN is quoted as 268°C compared with 250°C for PET (76), but this is well below the $T_m$ of CHDMT and thus fewer problems with thermal degradation are encountered. Incidentally, the homopolyester from NDA and CHDM cannot be made by a melt process, as it decomposes below its $T_m$ (77). However, significant differences do exist between the polymerizations of PEN and PET. Due to the stiffer molecular structure of the NDA ring, the melt viscosity of PEN is higher than PET for similar molecular weights. Because of the different rheology of PEN, higher polymerization temperatures must be used, up to 290°C. The catalysts used are similar to those used for PET.

Liquid-crystal polyesters are high performance, high added-value products that are derived from all-aromatic precursors and their raw materials are inevitably more expensive. 4-Hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) are both made by the Kolbe-Schmidt carboxylation reaction (78). In this reaction, the solid potassium phenoxide is heated under pressure with carbon dioxide. A major process improvement uses inert hydrocarbon oil as a heat-transfer fluid (79). Using phenol and 2-naphthol, respectively, HBA and HNA are made, although reaction conditions differ. 2-Naphthol can give both the 2,3- and 2,6-isomers depending on the alkali metal and the reaction conditions (80). Other LCP comonomers are 4,4′-dihydroxybiphenyl [92-88-6], hydroquinone [123-31-9], terephthalic acid, NDA, and 4-acetamidophenol [103-90-2]. The latter is used in certain high performance liquid-crystal polyesteramides, eg, VECTRA B [82538-13-4], (81). Hydroquinone (HQ) is manufactured on a large scale, much of it for photographic chemicals and the synthesis of antioxidants. There are several routes to hydroquinone, which are reviewed in an earlier volume of this Encyclopedia. The oldest route is oxidation of aniline to benzoquinone with manganese dioxide and its reduction to HQ. This process is obsolete and has been overtaken by other routes. The first is the alkylation of benzene or cumene with propene or 2-propanol in the liquid phase with a zeolite catalyst to a mixture of 1,3- and 1,4-diisopropyl-benzenes (82). These are separated and air oxidized to the hydroperoxides and decomposed into acetone and either HQ or resorcinol. The acetone can be reduced to 2-propanol and recycled via the alkylation stage (83). The latest process for HQ uses the direct oxidation of phenol with hydrogen peroxide and a strongly acid catalyst (eg, trifluoromethanesulfonic acid) to a mixture of HQ and catechol (84). Another process uses a special titanium zeolite with hydrogen peroxide to achieve the same result (85).

An important intermediate for liquid-crystal polyesters, particularly XYDAR, is 4,4′-biphenol or 4,4′-dihydroxybiphenyl. One route starts from 2,6-di-*tert*-butylphenol [128-39-2], which is oxidatively coupled (86) to 3,3′,5,5′-tetra-*tert*-butyl-4,4′-biphenol [128-38-1]. This intermediate is then dealkylated at high temperatures giving 4,4′-biphenol and isobutene. The isobutene is recycled to make more di-*tert*-butylphenol (87). An alternative route relies on sulfonation of biphenyl to the 4,4′-disulfonic acid and caustic fusion of the alkali metal sulfonate to biphenol. 4-Aminophenol and 4-acetamidophenol, which is the well-known analgesic acetaminophen, have been made for many years by two different routes. One starts with nitrobenzene [98-95-3], which is reduced to phenyl-hydroxylamine and rearranged in sulfuric acid to 4-nitrosophenol and the latter reduced to 4-aminophenol. The other route starts with 1-chloro-4-nitrobenzene [100-00-5], which is hydrolyzed to 4-nitrophenol, and then hydrogenated to 4-aminophenol. Since 4-aminophenol is highly susceptible to air oxidation, it is more convenient to use the *N*-acetyl derivative, which is chemically equivalent, during liquid-crystal polymerization. A newer acetaminophen process, originally developed by Hoechst Celanese Corporation, starts from phenyl acetate [122-79-2], which undergoes a Fries rearrangement in anhydrous hydrogen fluoride to 4-hydroxy-acetophenone, 4-HAP [99-93-4]. Beckmann rearrangement of 4-HAP oxime gives acetaminophen directly (88).

## 4. Manufacture of Polyesters: Polymerization Processes

Thermoplastic polyesters are step-growth polymers that need to be made to high molecular weight (12,000–50,000) to be useful (89). The first stage is an esterification or ester-exchange stage, where the diacid or its dimethyl ester is reacted with the appropriate diol to give the bis(hydroxyalkyl)ester and some linear oligomers. Water or methanol is evolved at this stage and is removed by fractional distillation, often under reduced pressure at the conclusion of the cycle. For ester interchange, weakly basic metallic salt catalysts are used: The list is extremely long, and many recipes are proprietary, but such salts as calcium, zinc and manganese acetates, tin compounds, and titanium alkoxides have been widely used (90–92). Certain ester-interchange (EI) catalysts have the undesirable effect of promoting thermal degradation at high temperatures (93) encountered during the latter stages of high polymerization. This is particularly true of PET and PEN. To overcome this, the EI-catalysts are sequestered at the end of the ester-interchange stage, frequently by adding phosphorus compounds, eg, triphenyl phosphite, triphenyl phosphate, or polyphosphoric acid in very small amounts (94). Again, such recipes are often proprietary. Titanium and tin compounds act as universal catalysts for both EI and polymerization reactions and are left unchanged. For the manufacture of poly(butyleneterephthalate), ester exchange using DMT and a titanium catalyst is the route of choice since butane-diol readily cyclizes to tetrahydrofuran (THF) in the presence of acids (95). Nevertheless, work was done on the direct polycondensation of butane-diol with terephthalic acid using special reaction catalysts and conditions to minimize THF formation (96–99).

The final polymerization stage is usually done in an autoclave fitted with a powerful mechanical stirrer to handle the viscous melt, under high vacuum at a temperature above the melting point of the final polymer. At this stage it is very important to eliminate oxygen and the process is blanketed with inert gas, nitrogen, or argon. During the polycondensation stage, the linear oligomers and the bis(hydroxyalkyl-terephthalate) esters undergo a succession of EI reactions, eliminating the diol that is removed under high vacuum, and thus molecular weight increases steadily. A polymerization catalyst is needed. For most polyesters, except those containing ethylene glycol units, titanium and tin compounds are suitable for both EI and polymerization, but for PET, (and PEN) antimony trioxide is the usual polymerization catalyst (100). It only becomes active at high temperatures and thus can be added at the start of the EI stage along with the other catalysts. In recent years, there has been pressure to move away from heavy metal catalysts like antimony, particularly in Europe, where they are viewed with increasing disfavor on environmental grounds. Problems have arisen in the United States with heavy metal contaminants (including antimony) in bottle waste glycolysis/methanolysis still-bottom residues. These cannot be land filled for environmental reasons and their safe disposal causes added expense. A less toxic metal would clearly be advantageous. However, alternatives are not easily found. Titanium alkoxides or alkyl-tin catalysts cause undesirable yellowing of PET and PEN, apparently due to complexation of the metal with thermally generated vinyl ester ends. This does not occur with PBT or with CHDM polyesters, since no vinyl ester groups are present. Germanium compounds (dioxide, tetra-alkoxide, or glycoloxide) are nontoxic and give very white polymers. However, they are too expensive due to the scarcity of the metal. Germanium or germanium–titanium mixtures are disclosed in a patent relating to PET bottles (101). A major advance was made by chemists at AKZO-Nobel in 1998 with the introduction of $TiO_2$–$SiO_2$ network catalysts (102–103). These are made by cohydrolysis or alcoholysis of titanium or zirconium alkoxides and silicate esters, a process familiar to ceramic chemists (104). The catalysts are very active and do not produce yellow colors with ethylene glycol polyester like PET or PEN. Thus a possible route to the environmentally desirable elimination of heavy metals in PET bottle resin opens up. Nevertheless, antimony trioxide is familiar, well understood, and robust as a polymerization catalyst. One drawback it does have in polymers such as PET is its susceptibility to reduction to metallic antimony, which can cause an undesirable gray color in the final polymer.

As the polymer molecular weight increases, so does the melt–viscosity and the power to the stirrer drive is monitored so that an end point can be determined for each batch. Melt polymerizations usually reach a point where the MW no longer rises with time but may being to fall, as degradation reactions overtake polymerization reactions. Usually, the polymerization end point is taken at a slightly lower molecular weight (MW) than this limiting value. When the desired melt-viscosity is reached, the molten polymer is discharged through a bottom valve, often under positive pressure of the blanketing gas, and extruded as a ribbon or as thick strands that are water quenched and chopped continuously by a set of mechanical knives. A new Du Pont process has eliminated the use of vacuum in melt polymerization by using a combination of advanced agitators designs and a brisk stream of inert gas, eg, nitrogen or carbon dioxide, to remove the volatiles (105–107).

Large amounts of PET are made by continuous polymerization processes and these will be discussed in much more detail when PET bottle resin are dealt with later. The PBT polymer is made both by batch and continuous polymerization processes (108–110). Increasing demand for PBT resins has led to older PET batch process plants being converted to manufacture PBT (111).

The polymer chip is dried thoroughly and stored for subsequent processing. Whenever a polyester is made by melt polycondensation, a small amount of cyclic oligomer is formed that is in equilibrium with the polymer. These oligomers can be extracted with solvents from solid polymer (xylene will remove the oligomers from PET in a simple Soxhlet extractor), but when the extracted polymer is remelted, more oligomer forms until the equilibrium is reestablished. The level of such oligomers is $\sim 1.4-1.8\%$ by weight for both PET and PBT. Thus it is not possible to completely remove cyclic oligomers from any melt-processed polyesters. In the case of PET, the main oligomer is a cyclic trimer (112–113) while in the case of PBT, the oligomers comprise roughly an equal mixture of cyclic dimer and trimer, together with much smaller amounts of higher oligomers (114). The presence of such oligomers usually does no harm, but under certain conditions they can exude to the surface. This is a recognized problem with polyester fibers, because it interferes with dyeing. Molded articles are not immune from oligomer deposition. For example, it affects the polymer surface and can mean trouble during electroless metal plating on metallized components, such as chromed plastic automobile door handles.

Polymers often must be made to much higher molecular weights than would be practicable by melt polymerization, either by reason of excessively high melt–viscosity or because degradation reactions overtake the rate of polymerization and the limiting molecular weight (see above) is simply too low. For very high IV polymer, solid-state polymerization (SSP) must be used. Dried polymer chip of moderate MW (IV 0.56–0.67) is heated at a temperature roughly 20°C below its softening point, either in a high vacuum or else in a stream of hot inert gas in a device that agitates the solid. Typical devices might be twin-cone rotary vacuum driers or a fluidized-bed unit using a blast of heated nitrogen or other inert gas to fluidize the bed of polymer chips. There are many commercial SSP units available and manufacturers constantly introduce new designs, notably in the bottle polymer market.

One important practical consideration, especially with PET, is that the polymer chips must be fully crystallized by thorough annealing before the start of the solid-phase polymerization. Usually, the polymer has been quenched in water from the melt before chipping, and as such it will be amorphous. If not precrystallized, the chips will sinter together on attempted solid-phase polymerization. The problems caused by several tons of polymer setting to a solid mass can well be imagined! The author is aware of one such incident many years ago, where the polymer mass had to broken out with jack-hammers! By careful annealing, one can raise the $T_{\mathrm{m}}$ of PET considerably above the usual figure (115), thus allowing the solid-phase polymerization to take place at higher temperatures and with shorter reaction times. Various agitation devices (116) and polymer chip treatments (117) have been described to prevent sticking. An integrated crystallizing and solid-state polymerization process has been described (118).

During the solid-state process, the volatile by-products of polycondensation (traces of water, methanol, excess diol, etc) escape by diffusion through the solid chip and are rapidly removed from the chip surface. Taking the usual PET chip size as $\sim 3$ mm, the volatiles only have to diffuse a distance of 1.5 mm to reach the chip surface. In a melt they have much further distances to diffuse and then have to form bubbles in a viscous ($\sim 3000$ P) melt. While diffusion through a solid is much slower than through a melt, the greatly reduced *distance* more than compensates for the slower *rate*. Esters of aliphatic diols and aromatic diacids start to slightly decompose by thermally cracking (even in an inert atmosphere) at $\sim 250^\circ$C (119). In the polymer melt, local shear heating by agitating the viscous melt can well exceed this threshold figure and thus cause degradation. Since SSP reactions are run at lower temperatures than melt polymerization, the balance in reaction kinetics between the polymer-forming and polymer-degrading reactions is more favorable and the outcome is a rapid molecular weight gain. The polymer chip is also further crystallized. For certain applications, it may be necessary to use chemical chain extension to increase the molecular weight of polyester by adding highly reactive diesters, eg, diphenyl terephthalate, which couples together hydroxyl-ended chains as terephthalate esters, evolving phenol as volatile by-product. This reaction goes readily at high temperatures (120), but is unsuitable for those products (eg, food containers), where traces of free phenol are highly objectionable. Final traces of phenol are remarkably difficult to remove. During polymerization reactions, various by-products are formed. In the case of PBT the major one is THF formed by dehydration of butane-diol or by internal cyclization the C4-ester units. This by-product is largely harmless as it is nonreactive under polymerization conditions and, being volatile, is quickly removed. The PET product by contrast has two major troublesome by-products. One is the generation of diethylene glycol (DEG) units in the chain by dehydration of 2-hydroxyethyl ester chain ends to form an ether link. This process cannot be prevented entirely and the concentration of DEG units is minimized by restricting time–temperature combinations that tend to favor DEG formation. The DEG content is related to the softening point by the empirical relation (121):

$$\Delta T_{\mathrm{m}} = (-2.2)M\,^\circ\mathrm{C}, \text{where M is the molar conc.of DEG}$$

As well as depressing melting point, DEG units have an adverse effect on the crystallinity of the polymer, reducing the strength of both fibers and oriented films and increasing the susceptibility of the polymer to chemical attack, especially aqueous alkaline hydrolysis.

The other major by-product is acetaldehyde, which is produced by pyrolysis of the PET unit. Random oxygen-alkyl scission of ester units leaves a vinyl ester end and a carboxyl-ended chain, the mechanism involving a McLafferty reaction (122). The vinyl ester reacts with another polymer end group to form a new polymer link and expel acetaldehyde, which is the tautomer of vinyl alcohol (123). The vinyl ester end can thermally polymerize to give chain-branched and cross-linked products and gel particles, and further thermal degradation of these polyvinyl units gives rise to colored polyenes (124,125). While acetaldehyde is highly volatile (bp $21^\circ$C), its presence is particularly objectionable in PET bottle resin used for soda bottles. Its presence cannot exceed 3 ppm in the final container if used for potable substances as it imparts an off-taste to popular cola drinks (126). The demands for low acetaldehyde levels can be even more stringent for certain bottled spa waters. Every time PET is melted during its processing, more acetaldehyde is inevitably generated and one reason for bottle resin undergoing a final solid-phase polymerization before the stretch blow-molding process is to remove the last traces of residual acetaldehyde.

Only the tiny amount of fresh acetaldehyde produced during the actual bottle molding process, which does not usually exceed 150°C, remains in the final article and this is within specification.

PTT (3GT) has its own peculiarities during polymerization and the process is distinctly different from that for either PET or PBT (56). Either ester interchange (EI) or direct esterification (DE) can be used with a suitable catalyst (127). Terephthalic acid is insoluble in propane-1,3-diol, but despite this, Shell (now Koch Industries) prefers the DE process on cost grounds (128). The process is carried out in two discreet steps. The first stage is an uncatalyzed direct batch esterification carried out under pressure. The boiling point of the propane-1,3-diol is 214°C and pressure raises the temperature to 250–270°C to dissolve the TA. The esterified mixture of low MW polymer and oligomers is then only partly transferred to the polymerization vessel, leaving a heel behind which is mixed with a fresh charge of raw materials for the next esterification run. Thus the esterification step is run in a batch-on-batch sequence. The polymerization is carried out in a separate vessel; using a tin, titanium, or zirconium catalyst at 260–270°C, the last stages being under vacuum. Since no vinyl ester ends are produced, yellowing with these metals is not a serious problem. However, there are still problems due to thermal degradation. The PTT polymer undergoes the usual McLafferty ester pyrolysis reaction, but this produces allyl alcohol and its oxidation product, acrolein. Both are toxic and acrolein is intensely irritant and lachrymatory. Antioxidants and stabilizers, eg, organic phosphites and hindered phenols, are added to minimize acrolein formation (128). German workers have described a technique whereby a titanium-silica catalyst (102–103) is used at the DE stage, and is then completely inactivated by adding a phosphorus acid. Antimony trioxide added as a polymerization catalyst. This technique greatly reduces allyl alcohol formation (129) and thus acrolein. Another thermal degradation product is ether-link formation from 3-hydroxypropyl ester chain ends and the production of bis (3-oxypropyl) ether groups (called DPG) analogous to the DEG linkages in PET. These lower the polymer $T_m$. A DuPont patent describes a staged polymerization process that minimizes the formation of both DPG links and allyl alcohol (130). The usual melt polymerized PTT has an IV of 0.70–1.00. Solid-phase polymerization can be used to raise the MW after annealing the polymer at 140–170°C. Two recent patents by Duh and co-workers describe in some detail improvements in the processes for SPP of PTT polymer (131–132). In the second of these patents, it is noted that PTT is less thermally stable than PET at high temperatures. The lower volatility of propane-1,3-diol means that PTT melt polymerization has a longer cycle time than PET for equivalent molecular weights. A problem peculiar to PTT is that quenched chips from the polymerizer extrudate are very friable and tend to crumble, resulting in a high content of fines (up to 15% w/w) on storage. It was found that using a chilled quench bath (0–18°C) made the chips tougher. If melt polymerized polymer is taken to a significantly lower IV (0.35–0.70), which means a shorter cycle time, and then subjected to SPP, the resulting high IV chips (0.80–2.00) are robust and much less friable, greatly reducing the fines problem. The PTT polymer crystallizes rapidly on quenching (its crystallinity is ~20% compared to 3–5% for PET) and because of this the polymer chip is insoluble in most common IV solvents. Shell prefers to use hexafluoroisopropanol (HFIP) as a solvent for IV determinations.

Polymerization of CHDMT is carried out in the melt, like PET, but there are important differences. The reaction temperature is significantly higher, as much as 310°C. Because the boiling point of CHDM glycol is so much higher than ethylene glycol, loss of diol by volatilization is not a serious problem and only a low molar excess of diol (5% molar) is needed to drive the polymerization to high MW. The EI route is preferred and, since vinyl ester ends are not formed, there is no yellowing problem with a titanium catalyst (eg, titanium alkoxides, such as tetraisopropyl titanate) for both ester exchange and polymerization stages. The final polymerization stage is run under high vacuum at 305–310°C. This is well above the previously mentioned thermolysis threshold temperature of 250°C. The CHDM molecule has two tertiary hydrogen atoms that are in a beta-position to the ester group, and hence prone to carboxylic acid elimination leaving a methylenecyclohexane structure. Thus CHDMT polymerizations operate rather more in a knife-edge mode than is the case for PET. This explains why antioxidants and stabilizers are important to CHDMT, and why the melt processing temperature window is much narrower.

The PEN polymer can be made like PET in either batch or continuous polymerization processes (CP) using ester exchange and a glycol ratio (mol EG to mol DMNDA) of between 1.5 and 3:1. In the CP process the reaction is run under moderate pressure to help dissolve the DMNDA in glycol. The ester exchange process is run in a series of steps from 170 up to 250°C under graduated pressure, 40 psig in the first stage, falling to 10–0 psig at the last stage where the viscous melt is transferred to the prepolymerizer. Polymerization is carried out in a series of temperature stages from 250 up to 290°C, ending with the high polymerizer or finishing stage where high vacuum is applied (133). The IV of the finished polymer is typically 0.49–0.53 dL/g.

The molecular weight of PEN can be raised by SSP, but as in the case of PET, the polymer chip (eg, from the CP unit) must be annealed and crystallized first. This is more complicated than a PET process. While PEN crystallizes rapidly under the correct conditions, because it has a high $T_g$ (125°C) and its vapor barrier properties are higher than those of PET, it is possible for the PEN polymer chips from the CP unit to contain trapped volatiles, eg, unreacted ethylene glycol, water, and traces of acetaldehyde. Annealing at high temperature could result in the sudden release of these volatiles. Hence a special devolatilization stage must be incorporated into the process before the chip can be fully annealed and crystallized ready for the SSP. The optimum PEN crystallization temperature range is 180–220°C, much higher than that for PET and the SSP temperatures are likewise higher (240–260°C). The final IV comes out typically at 0.55–0.70 dL/g (134).

Liquid-crystal polyesters are made by an entirely different route. Since they are phenolic esters, they cannot be made by direct ester exchange between a diphenol and a lower dialkyl ester. The usual method is the so-called “reverse ester exchange” or acidolysis reaction (135), where the phenolic hydroxyl groups are acylated first with a lower aliphatic acid anhydride (eg, acetic or propionic anhydride) and the acetate or propionate ester is heated with an aromatic dicarboxylic acid, sometimes in the presence of a catalyst, eg, potassium acetate. The phenolic polyester forms readily as the volatile lower acid distills from the reaction mixture. Many liquid-crystal polymers are derived formally from hydroxy acids (136,137) and their acetates readily undergo self-condensation in the melt, stoichiometric balance being automatically obtained.

Phenolic acetates frequently have convenient melting points and are readily purified by recrystallization. If the melting point of the acetate is too high, the propionate ester can be used instead. It is not necessary to isolate the acetates: Reaction of a mixture of diphenol, diacid, and/or hydroxy acid and acetic anhydride will generate the relevant acetates *in situ*, which then polymerize evolving acetic acid (138). In certain favorable cases (139) it is even possible to directly polycondense acids and phenols evolving water at temperatures $\sim 300^{\circ}$C. This process works well when catalyzed with compounds of Group IV (IVB) or V (VB) metals. Tin salts are suitable, notably dialkyltin dialkanoates or oxides (140). The process is less suitable for copolymers derived from 4-hydroxybenzoic acid, which readily undergoes decarboxylation $> 200^{\circ}$C. This does not affect the stoichiometry of polymerization as the phenol formed simply volatilizes away, but the polymer is left with less than the theoretical amount of HBA units. By contrast, hydroxy-naphthoic acid (HNA) is not decarboxylated under such conditions and copolymerization with non-HBA comonomers is possible by using direct esterification (141). Most of the commercial liquid-crystal polymers are made on a batch-wise process. Reaction temperatures are often very high: 360°C or even more. The high thermal stability of the arylate ester group allows such extreme conditions: Most LCP polymers do not start to degrade thermally below $\sim 480^{\circ}$C as measured by thermogravimetric analysis.

The liquid-crystal melt itself can lead to troubles during polymerization due to the extreme shear sensitivity of the strongly non-Newtonian melts. One annoying problem is “toffee-appling” in a stirred reactor vessel. Because of the high shear rate at the walls of the vessel, the molten polymer mass can adopt a form of rotary plug flow in which the whole mass revolves with the stirrer blade as if it were solid, like a toffee-apple on a stick! Thus no effective melt agitation takes place. This can be avoided by careful monitoring of agitator speed and the correct agitator blade design. Because of the low enthalpies of cooling for a nematic mesophase-solid transition, LCPs are readily quenched at extrusion from the polymerization vessel, but the ribbons or monofils can give problems at polymer chipping, due to the tough, fibrous nature of the polymer extrudate. The chips can come out of the cutter jagged or “hairy” due to fibrillation. This adversely affects feeding in extruder hoppers and is generally unacceptable to molders and processors. Various proprietary die-face cutters and melt handlers are available that can produce uniform polymer pellets from the molten polymer direct from the autoclave. These are very desirable for polymer drying and transfer. They feed well into screw extruders and molding machines since bridging problems in hoppers are avoided (142).

## 5. Blow-Molded Bottles

One of the largest single uses of PET resin, and certainly the most dramatic in growth during the last 20 years, is the stretch blow-molded PET soda bottle. In the food packaging business, the term Carbonated Soft Drink or CSD is the usual term for the contents of such bottles! Their annual consumption runs into billions of units in the United States alone, with corresponding rapid expansion on a worldwide scale. Poly(ethylenenaphthalene-2,6-dicarboxylate) is now also a significant polymer in food packaging, as will be discussed. The advantages of a blow-molded thermoplastic CSD bottle are self-evident: It is lightweight, shatterproof, and recyclable. The early market drive was reduction in weight, which reduced transportation costs at a time (early 1970s) when the United States was suffering from a severe energy shortage. Improved product safety associated with shatter-proof plastic bottles was another factor: recycling did not become a factor until somewhat later.

The major technical problem facing any thermoplastic bottle manufacturer is the permeability of the bottle wall to oxygen and carbon dioxide, which affects the shelf-life of the contents. The average 2-L CSD bottle maintains an internal pressure of roughly 5 atm of $CO_2$. To stop the carbonated product going “flat”, the $CO_2$ pressure must be retained during storage before unsealing for several weeks. Likewise, oxygen from the air must not diffuse in through the bottle walls to cause oxidation of the contents, thus spoiling the flavor of the product. Poly(ethylene terephthalate) is semipermeable, particularly when undrawn, and the first bottles experimentally manufactured used styrene–acrylonitrile copolymers (143). These were banned by the U.S. Food and Drug Administration (FDA) in the September 1977 due to traces of toxic acrylonitrile monomer present in the bottle walls, which could be leached out. Some early PET bottles had coatings of impermeable polymers such as poly(vinylidene chloride) or its copolymer with acrylonitrile applied to the outside. However, the process involved extra steps and the product was not readily recyclable (144). The most marketable bottle material is plain PET with a reduced permeability.

One extremely important development was the invention of the stretch blow-molded PET bottle process by Wyeth and Roseveare in 1973 (145,146). In this process, the polymer bottle wall is subjected to a rapid biaxial drawing stage that greatly increases its molecular orientation. Not only does this increase the mechanical strength of the bottle, but it also reduces the permeability of the walls to carbon dioxide diffusing out (147). The stretch blow-molding process was highly successful and following its introduction, the economic growth of the product has seen very high rates. While the 2- and 3-L CSD bottles have satisfactory shelf-lives of $\sim 3$ months, this is not always true of the smaller 1- and 0.5-L bottles due to their less favorable surface/volume ratios. The criterion for shelf life is the time to 15% loss of carbonation (147). However, in recent years as the popularity of PET bottles has grown, a large new market developed in uncarbonated bottled drinking water, which now forms a considerable fraction of the total bottle market, usually in the 50 cL (500 mL) size. Blow molded bottles are a very large industry worldwide. Some of the larger United States companies are Ball Industries, Constar (now part of Crown Cork and Seal) and Continental PET Technologies. Ball, for example, produced 5 billion bottle units in 2004 (148).

## 6. The Technology of Blow-Molding PET Bottles

Blow-molding thermoplastic hollow articles is a highly specialized process and for more details the reader should consult a specialist publication (149).

However, a brief outline of the process will be given so that the reasons for demanding certain polymer properties will be apparent. There are various processes in use, but the most popular is the two-stage or "reheat" blow-molding process. First, a bottle "preform" (sometimes called a "parison") is molded from PET by a conventional injection molding process. The preform looks like a large test tube with thick walls and the screw-cap threads and neck already molded in place. Multiple cavity dies are used to increase productivity. In the second stage, the preforms are heated in a mold cavity to a carefully controlled temperature above the glass–rubber transition temperature, typically to 90–100°C. The inside of the mold cavity is the size and shape of the finished bottle and the preform is subjected to a biaxial stretching process by a combination of mechanical deformation and air-pressure inflation. A hollow metal mandrel passes into the preform and partially elongates it in the axial direction; simultaneously dry air at ~50–100 psig is applied to blow the walls of the softened preform outward to fill the mold, thus giving radial stretching. The mold opens to allow the bottle to cool. This combined process results in both radial and axial drawing of the bottle walls that causes stress-induced crystallization and gives a container with superior strength, clarity, and freedom from environmental stress cracking. The kinematics of stretch-blow molding PET bottles were investigated by Cakmak and co-workers (150). They found that, depending on the mold temperature and inflation pressure, the preform inflated in either of two ways. In one mode, the preform ballooned out at the neck and the bubble traveled down the mold to fill it. In the other mode, the bubble formed half-way along the preform and expanded in two directions simultaneously to fill the mold. They estimated the high rates of deformation involved in this process could produce additional temperature rises of 15°C due to both adiabatic heating and stress-induced crystallization. The same authors also examined the morphology of the PET bottle walls in relation to blow-molding conditions (151).

The usual 2-L bottle preform weigh about 50 g and the final blown bottle has a wall thickness of ~0.015 in. (0.038 cm) (152). In view of the enormous number of bottles produced annually, the processes are constantly being modified to raise throughput rates and are all highly automated. There are many machinery manufacturers worldwide who specialize in the complex blow-molding equipment for PET bottles. Some examples are B & G Products LLC, Bekum International, Husky Injection Molding Systems, Jomar, Milacron, Nissei ASB Machine Co. Ltd., Sidel, SIG (formerly Krupp), and Kortec, who specialize in equipment for multilayer bottles. Typical cycle times for the actual blow-molding are 3–6 s. The process originally resulted in a bottle with a hemispherical base, which is clearly not suitable for standing upright on a refrigerator shelf! For several years PET soda bottles were fitted with separate flat bottomed base-caps, usually molded from high density polyethylene (HDPE) and secured with a hot melt adhesive. This meant extra cost due to extra material and extra processing steps and also interfered with recycling (153). The invention by Continental of the so-called "petaloid" base bottles with a five or six-lobed pattern base was a major advance: it made possible a one-piece, fully biaxially oriented bottle that would stand up by itself (154). This bottle design is now almost universal.

## 7. PET Bottle Resin Process

Stretch blow-molding is a mechanically severe operation with deformation rates up to 25,000%/min (150). The consumer wants a clear-glass bottle, any opacity caused by stress-induced crystallization is highly undesirable. The PET bottle resins are usually made to high MW (IV 0.75–0.92) so that the preforms can be blow-molded without problems. Such an intrinsic viscosity is too high for melt-polymerization and solid-stage polymerization is required. The process has been reviewed by Callander (155). In a typical PET bottle resin plant, the base polymer is made in a continuous melt-polymerization plant using either direct esterification of ethylene glycol with terephthalic acid or by ester interchange using purified dimethyl terephthalate (DMT), often partly recovered from recycled PET bottles. The illustration shows a schematic diagram of a plant using the terephthalic acid process (see Fig. 1).

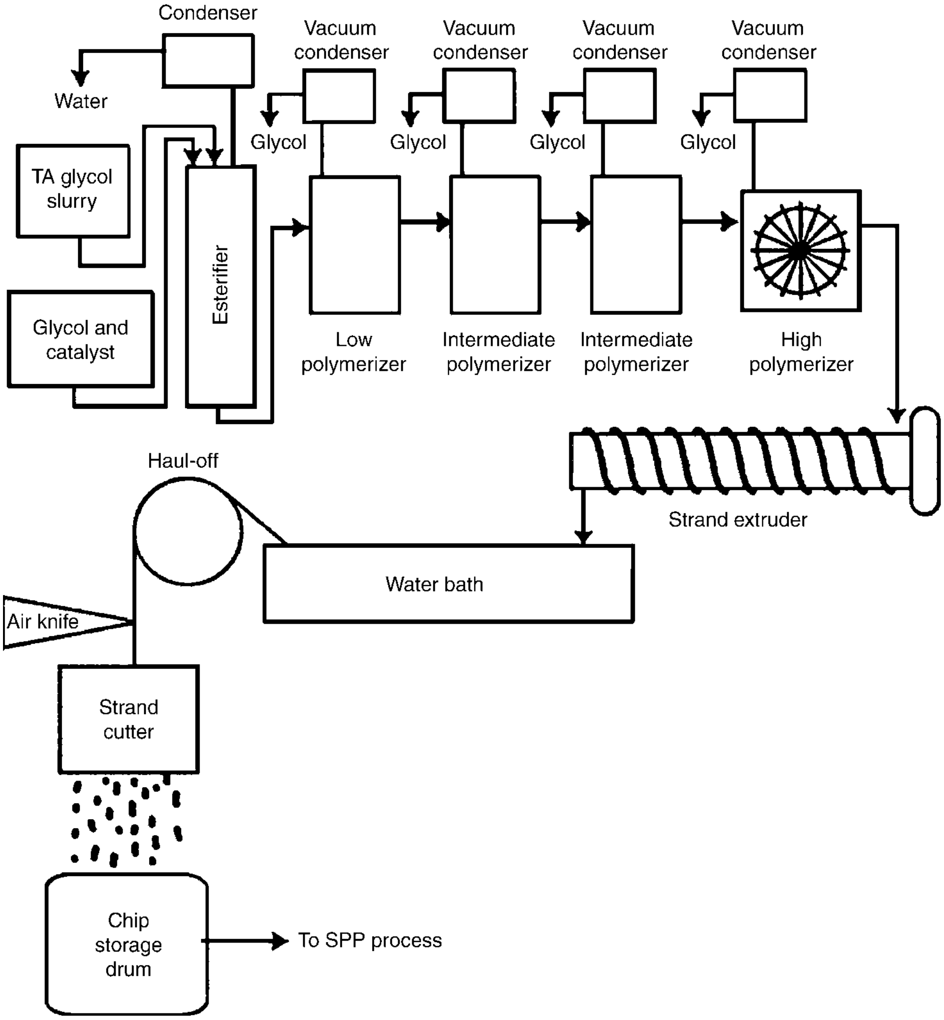


**Fig. 1.** A schematic diagram of a plant using the terephthalic acid process.

First, the terephthalic acid and glycol are thoroughly mixed to a paste and catalyst and stabilizers are added. The paste is pumped to the esterifiers where water is driven off and a molten mixture of bis(hydroxyethyl terephthalate) (BHET), oligomers, and low MW polymer is formed. This mixture is pumped through various polymerization stages: a prepolymerizer, an intermediate polymerizer, which on large plants is often itself divided into two or even three stages, and finally to the high polymerizer or finishing stage, where the polymer IV is $\sim 0.65$. During the various successive stages the melt grows increasingly viscous and high vacuum is applied at the finisher to complete the reaction. The agitators used in the polymerizers are highly specialized and proprietary designs built by specialist suppliers. The basic design principle is to provide maximum agitation to disengage the volatiles without high local shear rates and an absence of flow dead spots, where polymer melt could stagnate and undergo color-forming degradation reactions. Frequently, a wiped-wall falling film reactor is the basis of the final stage high polymerizer. At the exit from the high polymerizer, the molten polymer is extruded as multiple strands into a water bath and the quenched strands continuously diced to small chip $\sim 2.5$–3.5 mm across. The chips are then dried thoroughly down to a few parts per million (ppm) moisture content and passed to the crystallizers (sometimes these also have several stages), where they are annealed. This involves heating the chips gradually $> T_g$, gradually rising to a temperature close to the point of maximum PET crystallization rate ($\sim 170°C$). They are slowly agitated to prevent them from sintering together as they move to the final solid-state polymerizer. During the crystallization stage the chip density increases from 1.333 to $\sim 1.390\ g/cm^3$. Finally, the chips pass into the solid-phasing towers. Here they descend slowly under gravity in a plug flow mode through a long hot zone under a countercurrent flow of inert gas to sweep away the volatile by-products. The speed of descent is controlled so that optimum time–temperature profiles are maintained for the desired final IV. The scale of operation is impressive: large PET melt continuous polymerizers now run at 15–20 tonnes/h, which implies a maximum capacity of $> 300{,}000{,}000$ lb polymer per year. A large PET resin manufacturer may have several lines and can produce annually sufficient polymer to make several billion 2-L bottles.

The number average molecular weight for typical bottle resin is between 24,000 and 31,000 Da/molecule. As has been stated, acetaldehyde is the most objectionable by-product of PET polymerization, because it affects the taste of cola drinks at concentrations as low as 60 parts per billion (ppb). It can also affect the taste of bottled drinking waters. The specification for acetaldehyde in the final product must not exceed 3 μg of acetaldehyde per liter of headspace. The bulk of the acetaldehyde produced in the polymerization process is removed during the final SPP stage. Since blow-molding is carried out well $< 200°C$, only minute amounts of aldehyde are re-formed at the last stage. Originally, bottle preforms weighed 60–70 g, but this has been reduced to $\sim 50$ g. The lighter weight bottles naturally have thinner walls so that during biaxial drawing excessive stress-crystallization (opacity) again becomes a problem. As a result some manufacturers (156,157) have introduced copolymers of PET containing minor amounts (2–5 mol%) of such comonomers as isophthalic acid or cyclohexanedimethanol to reduce the polymer melting point by $\sim 4$–12°C with a correspondingly lower tendency to crystallize. This solves unwanted opacity problems. Another problem that may arise is a pearly appearance due to microvoids in the bottle wall. These are a result of mechanical degradation due to excessive deformation rates during blow-molding.

Polyesters hydrolyze rapidly at 280°C in the melt. Vigorous polymer drying to give chip moisture contents $< 50$ ppm is necessary before any melt processing, eg, the injection molding of bottle preforms. Some customers require colored bottles for their specific products; eg, certain popular non-cola sodas are packed in pale green bottles. Melt-dyed polymers using FDA approved dyes are used to mold the preforms for colored bottles.

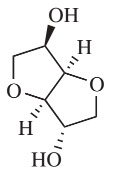
## 8. Hot Fill Applications

A growing market for blow-molded containers is the so-called hot-fill market. This covers wide-mouth bottles for such items as tomato ketchup, pasteurized fruit juices, and salad dressings that are packaged while still hot from the pasteurizer stage. The PET blow-molded bottle suffers from its relatively low $T_g$ (70°C), which results in severe bottle distortion if the temperature of the contents approaches $T_g$ (the maximum fill temperature is $\sim 60-65$°C). A brief heat treatment under constrained conditions at 160–220°C [analogous to the heat-setting stage during the drawing of PET fibers (see Fibers Survey)] will cure this problem, but introduces another process step (158). It can also cause another problem. While the oriented regions in the bottle remain clear, poorly oriented regions crystallize randomly and become opaque. However, Schmalbach-Lubeca have a introduced a True Heat process for annealing wide-mouth hot fill PET bottles, such as those used for pickles. These are filled directly from the pasteurization process. During blow molding, the amorphous PET regions are allowed to relax, which increases the degree of crystallinity in the ordered regions. A chilling step then freezes in the desired morphology (159). While this is one solution, the ideal answer would be a polyester with a higher $T_g$ than PET and PEN is one such polyester.

The PEN blow-molded bottles were first introduced in Japan (160). The PEN bottles received FDA approval for food containers in the United States in April 1996 (161,162). They have many advantages, despite their greater cost (at least four times that of PET). Poly(ethylenenaphthalene-2,6-dicarboxylate) has much better barrier properties than does PET (163). Its permeability to oxygen is five times less than that of PET and its permeability to carbon dioxide is nine times less. The $T_g$ is 125°C and tensile modulus is 50% higher than that of PET, making for greater stiffness. It absorbs ultraviolet (uv) light strongly $< 370$ nm and this is exploited in packaging light-sensitive materials, eg, vitamins (vitamin C is easily degraded by uv), baby foods, fruit juices and cosmetics, particularly in Japan. A recent publication shows that PET/PEN blend containers with only 4% PEN content gave significantly less degradation of vitamin C in apple juice irradiated with uv light (164). The photochemistry of PEN is such that it emits a violet fluorescence ($\sim 410$ nm), and the resulting Stokes shift is part of the mechanism by which the absorbed photochemical energy is degraded harmlessly before it can break chemical bonds. For some markets, this fluorescence is objectionable and one way of removing this is to copolymerize a halogenated aromatic moiety (eg, 4-bromonaphthalenedicarboxylate or 2-iodoterephthalate) into the polymer at low levels (1%) to quench the fluorescence by the "heavy atom" effect (165). The absorbed photochemical energy degrades by radiationless processes and emerges harmlessly as heat.

Poly(ethylenenaphthalene-2,6-dicarboxylate) is considerable more hydrolytically stable than PET due to various factors, eg, its high $T_g$ and a more hydrophobic nature. This means PEN containers can be reused and repeatedly steam sterilized. Production units for the raw materials for PEN, eg, NDA and DMNDA, are now fully on stream in several parts of the world. The PEN polymer is becoming become more cost competitive. Some manufacturers are examining PET/PEN copolymers, such as the Shell HiPERTUF high terephthalate copolymer. The $T_g$ of PET/PEN copolymers rises linearly with NDA content from the PET value (70°C) to that of pure PEN (125°C). However, only compositions with $< 15$ mol% NDA or $> 85$% NDA are semicrystalline. In the intermediate range, the copolymers are amorphous and molded bottles have poor barrier properties. Melt-blends of the two homopolymers are possible, but are complicated by the immiscibility of the two molten polymers. High shear mixing gives clear blends, but partial ester-exchange and randomization occurs (166). Japanese firms [Aoki Technical Laboratories (167)] have made clear blow-molded bottles using PET/PEN blends. Other approaches described use NDA polyesters or copolyesters made with other diols, eg, butane-1,4-diol (168), cyclohexane-1,4-dimethanol (169), or diethylene glycol (170) and alternative diacids, eg, *trans*-cyclohexane-1,4-dicarboxylic acid (171). These compositions are said to reduce oxygen and carbon dioxide permeability and to improve resistance to distortion in boiling water.

In the United States, one interesting recent approach to the hot-fill problem was made by DuPont, using copolymers of PET and isosorbide (172). Isosorbide is the bis(anhydrohexitol) derived from sorbitol, made by hydrogenating glucose. Isosorbide has two THF rings fused in a cis fashion with two hydroxy groups, so it is a rigid cyclic diol, easily derived from natural resources, already approved by the FDA in such drugs as isosorbide dinitrate and potentially inexpensive. Some early work on PET-isosorbide copolymers was done by Charbonneau and co-workers at Hoechst Celanese at Summit, NJ in the mid-1990s (173). The idea was to use the rigid diol to raise the $T_g$ of PET copolymers to $\sim 85-90$°C and thus provide a simple answer to the hot fill problem. Unfortunately, the problem is the lack of reactivity of isosorbide, which is a bis secondary alcohol and has one *endo* and one *exo* hydroxyl groups of widely differing reactivities.



Isosorbide

Much of the added isosorbide is simply lost during the polymerization and only a small fraction actually incorporated. DuPont continued the work and showed that the bis(hydroxyethoxy) ether of isosorbide could be copolymerized without trouble, but did not significantly raise $T_g$ (174). The best approach appears in more recent DuPont patents where an amorphous isosorbide homopolymer with terephthalic acid or isophthalic acid is made separately, and then melt blended with PET to form a randomized copolymer. In this way, relatively large amounts of isosorbide can be incorporated. Using a melt blend of 80 parts PET and 20 parts poly(isosorbide isophthalate) gave a polymer with a $T_g$ of 94°C. The calculated actual isosorbide level [from nuclear magnetic resonance (nmr)] was $\sim 7.5$ mol% (175).

## 9. Bottles for Beer, Wine, and Other Demanding Contents

For plastic bottles holding liquids like beer and wine, the demands are far more severe than for the CSD market. In the former case the problem is keeping carbon dioxide *in* the bottle; in the case of beer or wine, it is far more important to keep oxygen *out*. Oxygen permeability of polyesters is a problem. Glass bottles give a perfect hermetic seal; which PET bottles patently do not. The PEN bottles have lower oxygen permeability (176) and offer one solution, but they are too expensive for "single serve" or "one-trip" bottles. Unlike PET bottles, they can be sterilized at high temperatures many times over, due the better hydrolytic stability of PEN and reused. Brewers in Denmark introduced their beer in returnable PEN copolymer beer bottles in 1999 and a 1.25-L beer bottle was launched by Rexam Petainer for sale in Norway, but both these are countries where recycling and bottle return is widely practiced (177). For high barrier one trip bottles, people are looking to coated or multilayered bottles to reduce oxygen permeability. A recent review by Grande covers the various technical options available for achieving high barrier property polyester bottles and containers (178). There is at the time of writing no clear winner in the race for the ideal barrier bottle: instead the solutions adopted depend very much on the individual circumstances. The main classes of solutions would seem to be (*1*) new bottle resins; (*2*) barrier coatings; (*3*) oxygen scavengers; (*4*) multilayer bottles with barrier zones; (*5*) nanocomposites.

According to the Grande article (*loc.cit*), the current technology balance for barrier bottles is 62% multilayer, 25% monolayer, and 13% coatings. The measure of success is the shelf life of the bottle contents and its presentation in an acceptable form to the consumer. There is much activity in Europe at the moment in the plastic beer bottle market and it is possible that even the familiar aluminum beer can may be under threat. The PET soft drink and water bottles have largely eliminated other container materials in their respective fields, so a ready market awaits. Already 10% of beer consumed in Europe comes in PET bottles. In Korea, the Hite Brewery Company claims that 15% of all beer consumed in South Korea comes in 1.6-L multilayer PET bottles with a shelf life of 26 weeks. In the United States, the first cautious steps have been taken by Anheuser Busch and Coors in supplying their beers in 16-oz (453.5 g) multilayer PET bottles.

Multilayer bottles are blown from an injection-molded multilayered preform. The barrier layer material most often mentioned is MXD-6. This is an aromatic polyamide made from adipic acid and *m*-xylylenediamine, which comes from the hydrogenation of isophthalonitrile, in turn readily availble by ammonoxidation of *m*-xylene. The MXD-6 polyamide has been known for many years and has very good barrier properties. Descriptions of the injection molding process for multilayer parisons (preforms) of three and five layer bottles can be found in the patents of Beck (179), Krishnakumar (180), and Collette (181). The Collette patent describes a PET/MXD-6 combination, which is said to be clear and recyclable as the amount of MXD-6 is small. Dow Chemicals announced in 2000 an amine cured epoxy barrier film for multilayer PET bottles under the name BLOX (182). It was said to give excellent clarity and adhere very well to PET, but the product has since been discontinued (183). The Collette patent also describes the use of catalytic cobalt salts in the MXD-6 to act as an oxygen scavenger. This system was developed by Crown Cork and Seal Co under the name OXBAR. Other oxygen active scavenger systems for use in food packaging have been described, eg, ascorbic acid (Vitamin C) and iron compounds (184). For further references to oxygen scavenging systems (see FOOD PACKAGING).

Coated bottles embrace both organic and inorganic coatings, the latter being more successful. The two chief materials in use are amorphous carbon as in the Sidel Group's ACTIS plasma coating process and amorphous silica ($SiO_2$) is used by SIG Corpoplast who have a proprietary Plasma Impulse Coating Vapor Deposition (PICVD) process that deposits a silica coating, $< 0.1\,\mu$ thick, on insides of PET bottles. The process runs at 10,000 bottle/h (178). This coating raises the shelf life of the PET 12 oz (140.1 g) CSD bottles to $> 25$ weeks. The very thin inorganic coatings do not affect bottle clarity or recycling. Another barrier system is based upon nanocomposites. These are polymer dispersions of the minute silicate sheets derived from exfoliated clays (clays treated with organic quaternary ammonium salts to replace metal cations present in the layered clay structures). Such nanodispersions have greatly reduced gas permeability. One such is Imperm nanoclay/MXD-6 blend for use in multilayer PET bottles, developed by Mitsubishi Gas Chemical, who also produces MXD-6 polyamide. The nanoclay further boosts the impermeability of MXD-6.

Finally, work is still going on to find more impermeable polyesters for single-layer blow-molded bottles. One interesting idea comes from Futura Polyesters in India. They are using a blend of PET with polytrimethylene naphthalate (PTN or 3GN). This novel polyester has 18 times the $CO_2$ barrier properties of PET and 3.5 times that of PEN, and 9 times the $O_2$ barrier of PET and twice that of PEN. It is claimed that PET/PTN blend beer bottles cost no more than glass and are much lighter and shatterproof. Four major Indian breweries are evaluating the new bottles (185).

## 10. Economic Aspects

The total world market for PET bottle resin is still growing at a rapid rate. A survey indicated that the annual growth rate worldwide exceeded 15% per annum in the 1990s and one article (186) stated that the global consumption of PET grew at 19% during 1992. Much of this growth was due to the demand for PET bottle resin. Since then the demand has continued to climb at a more modest rate. The total devoted to CSD bottles is very large and the United States

Table 1. **U.S. Beverage Container Market Survey**[a]

| Material | 1997, billion units | 2002, billion units | 2007, billion units |
|---|---|---|---|
| plastic | 35 | 52 | 70 |
| metal | 99 | 100 | 102 |
| glass | 28 | 26 | 30 |

[a] *Source*: Ref. 188.

is the largest consumer, with Europe next. China is now advancing rapidly with the high economic growth of that nation. According to a recent review of plastics in packaging in China, by Hoggard (187), the annual growth rate for PET CSD bottles was 18% from 2000–2005. Hot-fill bottles grew at 50% per annum. There is a potential market for 25–30 billion PET beer bottles per annum in China where the annual production of beer was 20 million tonnes in 2000! The annual output of all plastic packaging materials (including PET bottle resin) was 9.5 million tonnes in 2005 and is expected to rise to 13.7 million tonnes by 2008 (further breakdown of figures was not available).

Globally, there are many interesting market variations, notably the strong demand for packaging for mineral waters in Europe and the large hot-fill market in Japan, compared with the United States. Future strong growth of PET bottle demand looks to be assured, its balance of properties and ability to be recycled being major factors. A market survey of the U.S. beverage container market 2002–2007 (188) shows that the market for plastic bottles (largely PET) is still growing, while glass and metal cans are more or less static or slightly in decline (see Table 1).

The U.S. market price for PET bottle resin in bulk in May 2004 was 63 c/lb (189).The main manufacturers of PET bottle resin in the United States are planning to add to their resin capacity in 2005–2007 as shown in the Table 2 (190).

## 11. Recycling Bottles

The whole topic of recycling materials is a vast one and is covered in more detailed terms in an article in this Encyclopedia. However, it is entirely appropriate to deal at least in outline with the specific question of PET (and other polyesters) CSD bottles as they are a huge volume market and the very word

Table 2. **U.S. Bottle Resin Capacity Expansion 2005–2007**[a]

| Manufacturer | Planned increase, million lb | Year |
|---|---|---|
| Eastman Chemical Co. | 500 | over 2005–2007 |
| Wellman Industries | 290 | 2006 |
| DAK Americas Inc. | 210 | 2006 |
| M & G Group (Italy) | 90 | 2005 |
| StarPET Inc. | 50 | 2005–2006 |

[a] *Source*: Ref. 190.

Table 3. **U.S. Gross Recycling Rate for PET Containers**[a]

| Year | Total U.S. bottles collected, million lb | Bottles on U.S. shelves, million lb | Gross recycle rate, % |
|---|---|---|---|
| 1995 | 775 | 1950 | 39.7 |
| 1996 | 697 | 2198 | 31.75 |
| 1997 | 691 | 2551 | 27.1 |
| 1998 | 745 | 3006 | 24.8 |
| 1999 | 771 | 3250 | 23.7 |
| 2000 | 769 | 3445 | 22.3 |
| 2001 | 834 | 3768 | 22.1 |
| 2002 | 797 | 4007 | 19.9 |
| 2003 | 841 | 4292 | 19.6 |
| 2004 | 1003 | 4637 | 21.6 |

[a] *Source*: Ref. 191.

recycling is popularly associated with PET bottles! A very good source of information is the 2004 Final Report on Post Consumer PET Container Recycling, produced in 2004 by the National Association for PET Container Resources (NAPCOR). This only deals with the U.S. market, but this is the largest in the world at the time of writing (191). The report points out that through 2004 the rate of growth of PET containers was still 8% higher than for 2003, largely as a result of double digit growth in PET bottles for water and isotonic sports drinks. The introduction of 12 oz (140.1 g) CSD bottles was also a factor. The NAPCOR estimate of the total PET bottle and jar potential for recycling in 2004 was 4.637 billion lb. This figure allows for PET bottle resin used in the United States, imported and recycled resources, less exports. The total material recycled was 1.003 billion lb, representing a recycle rate of 21.6%. The recycling rate in the United States has tended to fall steadily since 1995 on a yearly basis and Table 3 shows a summary of the years 1995–2004. It seems as if the collection rate is fairly constant ~ 770 million lb, but the rise in production has not much affected the former.

The total U.S. capacity for recycling in 2004 was 937 million lb distributed among thirteen plants or facilities. The price of PET bottle chip in 2004 varied from a low of 13c/lb to a high of 18 c/lb. The largest use of recycled PET bottle chip (54.5%) was PET fiber, either as fiberfill or in PET contract carpets. Food containers took 14.3%, strapping and slings took 13.2%, nonfood containers took 7.2% and sheets and film took 6.6%s. While there was a rise in use of recycled PET in engineering resins, the total amount was tiny, only 1.4% of the total.

As newer materials come into use, the problem obviously arises how are they to be recycled and integrated into a recovery system. One problem is posed by PEN or PEN/PET blend or copolymer bottles if they ever become a high volume market. Both PEN and PET are not compatible in recovery streams. The problem has been long anticipated and a X-ray sensor to separate PVC from PET was devised at Rutgers University Centre for Plastic Research in 1989. A paper at the Novapak 1997 Conference (192) detailed work by Kenny and Roe of MSS Inc. on devices to separate PET and PEN-containing bottles. Problems encountered were the presence of food residues in the containers, old paper labels and dirty bottles that confounded the earlier devices. However, a second generation sensor array gave much better selectivity and with clean, delabeled containers ought to be almost 100% selective.

## 12. PET Molding Resins

It is difficult to establish the exact breakdown of the world demand for PET as a molding resin from the open literature. The total tonnage is small compared with the vast amounts used for fibers and bottle resin. The bulk of the U.S. market for PET molding resin is the auto industry. Recently, a survey of the North American market for all molded polyesters in 2003 indicates a figure of 96 million lb for PET (see the section on PBT). Its $T_m$ and heat distortion temperature are higher than those of PBT and its low moisture uptake and dimensional stability with changes in humidity, make it superior to nylon. Both PET and PBT engineering resins have good resistance to chemicals and being semicrystalline, do not suffer from solvent stress cracking, which plagues amorphous materials such as polycarbonate. Polyesters are only attacked by severe chemicals, eg, powerful acidic or phenolic solvents, hot strong aqueous alkali, and certain bases (hydrazine).

In the unfilled state, PET is not a good molding resin and all commercial grades are filled with either chopped glass strand (1/8 in. or 3–4 mm long) or mineral fillers (usually mica) or a mixture of the two. Various proprietary nucleating agents are added; these are often sodium salts of various organic carboxylic acids (see previous references). Some manufacturers supply fire-retardant polymer grades as well. Such formulations often involve a synergistic mixture of an aryl halide with antimony oxide (see Flame Retardants Overview). One difficulty with flame-retardant PET polymer is that recipes that contain antimony trioxide can suffer severe polymer degradation at molding temperatures $\sim 280–290^\circ$C.

As discussed earlier, antimony trioxide, which is a polymerization catalyst, also acts as prodegradant at high temperatures. This is a less serious problem with FR grades of PBT due to the lower processing temperatures involved (240–250°C). To mitigate the PET problem, pentavalent antimony compounds like sodium antimonate are used in some FR formulations. The halogenated species is often a ring-brominated polystyrene (193–198). These materials are approved for Underwriters Laboratory V-0 classification and have the advantage that, being polymeric, are nonfugitive and less likely to be environmentally harmful than small molecule additives, eg, decabromopdiphenyl oxide. Nonetheless, there is much pressure, particularly in Europe and Japan, to remove halogenated aromatics, notably the polybrominated diphenyl ethers (PDBEs) on environmental grounds and this tendency is spreading to the United States (199).

In the 1990s in the United States, there was pressure on manufacturers from the automotive industry, led notably by the Ford Motor Company, to use at least 25% by weight of Post Consumer Recycled (PCR) material in their resins rather than 100% virgin polymer. In the case of PET, this was readily achievable due to the large volume of recovered PET bottle polymer chip available in the United States and in Europe. An article (200) states that during 1993, as much as 418 million lb, 41% of all the PET CSD bottles used in the United States, was recycled. However, since then, this figure has somewhat fallen away (see the section on PET Bottle Recycling). Such material certainly counts as PCR polymer, and some suppliers use 100% recycled polymer in their compounded PET resins. The PCR recovery process and subsequent melt compounding and reformulation reduce the initial IV of the original PET bottle resin from ~0.75–0.85 to values more like 0.62–0.65, but this is still in the range of virgin melt-polymerized resin, as opposed to SSP resin. In the auto industry, the majority of the components are pigmented black, so differences in feedstock PCR chip color are less important. If pale-colored resin is specifically needed for an end use, then virgin polymer may be necessary.

In the early days, PET moldings were used in small components, notably electrical connections and covers for switchboxes or fuses. This is still important today, even more so with the growing complexity of the modern automobile with its numerous on-board electronics, but recently the trend has been to use PET moldings more and more for nonload-bearing structural parts, eg, radiator grille supports and headlamp mountings. Glass/mineral filled PET moldings do not have a smooth enough surface (Class A Finish) for exterior body parts that would show. However, they are very suitable for internal structural components. As part of the trend begun to reduce automobile weight to improve gas mileage, this continues even if better gas mileage has been somewhat forgotten during the surge in popularity of heavy truck-like vehicles like SUVs in the United States. Despite this, the amount of plastic used in automobiles is still rising. Figures published recently show that the weight percent of plastics and composites in the average North American vehicle rose from 4.6% in 1977 to 7.6% in 2003 (201). Some of the moldings are dimensionally quite large, weighing 10 lb per shot. Improvements in mold design and better understanding of flow behavior in molds, brought about by increasing use of computer-aided design and flow-simulation programs have all helped to make these large moldings possible on a routine production basis. Another factor is the increasing use of robots in molding shops. Such large structures are removed hot from the mold by robots and clamped to a jig to cool to ensure no distortion or warpage takes place during the cooling cycle.

## 13. Physical Properties of PET

The full crystal structure of PET has been established by X-ray diffraction (202–205). It forms triclinic crystals with one polymer chain per unit cell (see Table 4). The original cell parameters were established in 1954 (202) and numerous groups

Table 4. **Crystal Structure of PET (Triclinic)**

| Parameter | Value and unit |
|---|---|
| $a$ | 0.444 nm |
| $b$ | 0.591 nm |
| $c$ | 1.067 nm |
| $\alpha$ | 100° |
| $\beta$ | 117° |
| $\gamma$ | 112° |
| calculated crystal density | 1.52 g/cm$^3$ |

have reexamined it over the years. One difficulty is determining when crystallinity is fully developed. Kitano (205) annealed PET at up to 290°C for 2 years.

Thermochemical data depends on the degree of crystallinity in the polymer and a very highly annealed polymer sample can have $T_m = 280°C$, much higher than the usual value of 260–265°C (206). The heat of fusion (207) is ~140 J/g (33.5 cal/g). The glass–rubber transition temperature ($T_g$) depends both on the method of measurement and the state of the polymer. A solid chip sample as measured by Differential Scanning Calorimetry (DSC) gives a value ~78°C (208), but a highly oriented and crystalline drawn fiber measured by the dynamic loss method will give values as high as 120°C (209,210). By the same token the specific gravity of undrawn amorphous PET is 1.33 while crystalline drawn fiber has a value of 1.39.

As a step-growth polymer made under equilibration conditions, PET has a molecular weigh distribution very close to the theoretical value of 2.0. The Mark-Houwink equation relates the intrinsic solution viscosity to the molecular weight by the relation:

$$[\eta] = K.M_V^{\alpha}$$

where $M_V$ is the viscosity average molecular weight and $K$ and $\alpha$ are the Mark-Houwink coefficients, determined experimentally for individual solvents. The usual solvents historically used for PET are 60:40 w/w phenol/tetrachlorethane (P/TCE) and 2-chloro-phenol (OCP). Neither solvent system is entirely satisfactory and better results have been obtained using either hexafluoroisopropanol (HFIP) or a 50 : 50 by volume mixture of HFIP and pentafluorophenol at 25 °C (211). Although expensive, these acidic fluorinated solvents readily dissolve even highly crystalline samples of PET at moderate temperatures, thus avoiding the degradation problems commonly encountered with the older solvents at high temperatures. Degradation under normal conditions is minimal. The Mark-Houwink coefficients for PET for a range of solvent systems are shown in Table 5.

As stated, PET does not crystallize well in the unoriented state even in a hot mold unless nucleating agents and/or plasticizers are added. Commercial PET molding-grade polymers are nearly always filled and typical compounded polymer properties are set out in Table 6.

## 14. Economic Aspects

The first company to introduce nucleated PET molding resins was Akzo Plastics BV with their ARNITE range (this business was later taken over by DSM NV).

Table 5. **Mark-Houwink Coefficients for PET in Various Solvents at 25°C**

| Solvent | $K$ in dL/g | $\alpha$ |
|---|---|---|
| OCP | $6.31 \times 10(-4)$ | 0.658 |
| P/TCE | $7.44 \times 10(-4)$ | 0.648 |
| HFIP | $5.20 \times 10(-4)$ | 0.723 |
| PFP/HFIP | $4.50 \times 10(-4)$ | 0.705 |

Table 6. **Typical Properties of PET Molding Resins**[a]

| Parameter[b] | ASTM method | 30% Glass | 45% Glass | 35% min/glass | 35% min/glass |
|---|---|---|---|---|---|
| sp. gr. | D792 | 1.58 | 1.70 | 1.60 | 1.60 |
| tensile | D638 | 24,000 psi | 28,500 psi | 14,000 psi | 15,000 psi |
| elongn. | D638 | 2.0% | 2.0% | 2.2% | 2.1% |
| flx at 5% | D790 | 35,000 psi | 45,000 psi | 21,500 psi | 22,000 psi |
| flx mod | D790 | 1.4 Mpsi | 2.1 Mpsi | 1.4 Mpsi | 1.4 Mpsi |
| Izod, N | D256 | 1.5 ft·lb/in. | 2.0 ft·lb/in. | 1.1 ft·lb/in. | 1.1 ft·lb/in. |
| HDT at 264 psi | D648 | 224°C, 453°F | 229°C, 444°F | 202°C, 396°F | 216°C, 421°F |
| Flamm | UL94 | HB | HB | HB | HB |
| DS 1/8 in. | D149 | 565 V/mil | 540 V/mil | 500 V/mil | 450 V/mil |
| DS 1/16 in. | D149 | 904 | 631 | 550 | 575 |
| DS 1/32 in. | D149 | 975 | 951 | 810 | 860 |
| VR 23C 50% RH | D257 | 3.0 × 10(15) |  | 1.0 | 1.0 |
| $\varepsilon$ 10(3)Hz | D150 | 3.2 | 3.5 | 3.8 | 3.8 |
| $\varepsilon$ 10(5)Hz | D150 | 3.1 | 3.4 | 3.6 | 3.7 |

[a] See Ref. 212.

[b] Dielectric strength = DS; VR = Vol. Resisitivity, $\varepsilon$ = dielectric const.

DuPont introduced their RYNITE fast-crystallizing materials in 1978, followed by other manufacturers. The present North American market is dominated by DuPont Plastics, no doubt by virtue of their early lead, but other suppliers are Allied-Signal (now Honeywell) with PETRA and Hoechst Celanese Corporation (now Ticona) with IMPET. Eastman also market PET injection molding grades under the trade-name THERMX. In Europe the situation with PET is confined primarily to two suppliers, DSM NV and Du Pont, while in Japan the main suppliers are Teijin, Toray (Du Pont) and Toyobo (see Table 7).

## 15. Safety and Environmental Factors

The PET polymer is safe and poses no threat to animals or humans. Its fibers have been in use for > 40 years and PET has FDA approval for use as a food packaging material. The PET fibers have been used in interarterial prostheses. The only major hazard in handling PET resins is the dust hazard associated with mineral or glass fillers during chip grinding or compounding operations. Appropriate protective equipment must be worn. All extruders or machinery handling molten polymer should be properly ventilated to remove harmful fumes from the

Table 7. **Current Prices for PET Molding Resins**

| material | > 1 million lb | 300,000–500,000 lb |
|---|---|---|
| PET injection | 96–101 c/lb | 106–116 c/lb |
| PET 30% glass FR | 133–143 c/lb | 143–153 c/lb |

stray decomposition of molten polymer. Molten PET causes serious thermal burns in contact with bare flesh; adequate thermal protection, eg, heat-proof gloves should always be worn when handling hot polymer.

## 16. PCT Molding Resins

Another thermoplastic polyester on the scene is PCT, CHDMT, poly(cyclohexyldimethyleneterephthalate), first produced by Eastman Kodak some 50 years ago as a polyester fiber (loc.cit.). The PCT resin was introduced as a molding resin in 1987 in glass-filled and flame-retarded grades with specific end uses in mind (213). Eastman are the sole polymer suppliers from their plant in Kingsport, Tenn., although some polymer is believed to have been supplied to General Electric who marketed it as part of their VALOX range of thermoplastic polyesters. The targeted end uses appear to be connectors for both the electronic and the automotive markets. The PCT polymer is significantly less expensive than the ultrahigh performance LCP engineering resins (see later). One specific advantage of PCT is that it has very similar flow characteristics during injection molding as both PET and PBT, albeit at significantly higher temperatures. This means that extensive mold and runner redesign is unnecessary: PCT is a drop-in substitute polymer and this quality alone makes it highly attractive to molders.

About 15 years ago, a new development came along in the electronic industry associated with miniaturization. This was the so-called surface mount technology or SMT (214,215). It took over a significant part of the assembly process in electronic circuitry. There is a lower level of penetration of this technique in the automotive electronic component market, but its use here is growing. The SMT process uses a solvent vapor heated reflow soldering process. Whole arrays of electronic components are mounted in preset positions on printed circuit boards with accurately prepositioned solder balls ready to make connections. Immersing the whole board in a hot vapor bath melts the solder and allows it to flow, thus completing many individual circuits in one operation. For the usual 60:40 tin/lead electrical solder, the vapor temperature is usually about 215°C (420°F). This puts great thermal demands upon thermoplastic parts and as a result, the “blistering” temperature of these components has to be well above the soldering bath temperature. This is beyond the capability of PBT and most nylons, except nylon 4:6. Interestingly, the HDT value is *not* a very precise guide to performance in the blistering test, although obviously the higher the HDT, the better. PCT has a HDT $\sim$260°C (500°F) and its blistering performance under vapor reflow soldering conditions is excellent.

Lately, with the new millenium, a new situation has arisen. The drive to eliminate lead-based solder from all electrical and electronic consumer equipment in Japan and Europe has led to the so-called Waste Electrical and Electronic Equipment (WEEE) legislation. After July 1, 2006, no consumer products containing lead solder can be sold in such countries. This has meant a major revamp of vapor phase soldering material specifications. The acceptable replacement lead-free (LF) solder is a eutectic 96:4 tin–silver alloy that melts at 221°C, much higher than the melting range of the tin–lead solders ($\sim$185°C). This

Table 8. **Properties of CHDM**

| property | *cis*-CHDMT | *trans*-CHDMT |
|---|---|---|
| melting point, $T_m$ | 251–256°C | 312–318°C |
| glass rubber transition, $T_g$ | 60°C | 95°C |

means that the vapor-phase reflow soldering operation will need bath temperatures ~250°C or higher. This is approaching the blistering temperature of existing PCT compositions, but it may make PCT even more attractive vis-à-vis other polyesters and thermoplastics. The change may provide big market opportunities for more heat resistant (but expensive) thermoplastics, eg, LCPs. The implications of the move to LF soldering for SMT components has been recently reviewed by F Liotine (216).

## 17. Physical Properties of PCT (CHDMT)

The properties depend on the exact ratio of cis to trans isomers present, but these are approximately linear with respect to isomer ratio (see Table 8).

## 18. Crystal Structure of CHDMT Pure Isomers

The table of crystal parameters is shown in Table 9. Both isomers of CHDMT exist in a triclinic system with the *c* axis more skewed in the case of the cis isomer. Copolymers of the two forms show a gradual distortion of the crystal lattice from one form to the other, which is why there is no minimum melting or eutectic point (217).

The PCT has low moisture uptake and (unlike nylon) is not affected by changes in humidity. However, as with all high melting polyesters, care must be taken to dry the polymer chip thoroughly before melting. The PCT polymer has both a high melting point (285–290°C) and a high melt–viscosity. Processing temperatures have to be > 300°C, which is high for non-LCP polyesters. The combination of properties can lead to thermal and thermooxidative degradation and severe IV drop during molding, giving brittle parts (218). The presence in the molecule of two tertiary hydrogen atoms both in a beta-position to the ester

Table 9. **Crystal Structure of cis and trans CHDMT**

| Parameter | Pure cis isomer | Pure trans isomer |
|---|---|---|
| $a$, nm | 0.602 | 0.637 |
| $b$ | 0.601 | 0.663 |
| $c$ | 1.370 | 1.420 |
| $\alpha$, deg | 89.1 | 89.4 |
| $\beta$ | 53.1 | 41.1 |
| $\gamma$ | 112.5 | 114.4 |
| calculated crystal density, g/cm$^3$ | 1.303 | 1.265 |

group has already been mentioned. Several patents have recently appeared on the use of extra additives, antioxidants and other polymer stabilizers to overcome this problem (219–221). Another recent patent describes copolymers (222) with better crystallization rates and molding properties, and two patents have appeared on the use of terephthalic acid in place of dimethyl terephthalate in the production of the polymer, both in batchwise (223) and continuous polymerization processes (224). The new family of PCT resins was originally called EKTAR, but is now redesignated THERMX since the reorganization of Eastman Chemicals into an independent corporation.

## 19. Properties of PCT

As indicated earlier, PCT is in effect a copolymer of terephthalic acid with two diols, the cis and trans forms of cyclohexanedimethanol. These two isomers do not form a eutectic copolymer with a minimum melting point, but instead the melting point rises monotonically between the two $T_m$ values of the pure isomeric homopolymers (225). The pure cis polymer melts at ~250°C and the pure trans polymer at ~305°C. The $T_g$ values likewise rises from ~60°C (cis) to ~95°C (trans). There is little difference in the degrees of crystallinity or crystallization rates over the composition range, which means that variations in isomer ratio do not have a marked effect on the physical properties of the polymer. The usual commercial form of PCT has an isomer ratio of 70:30 trans/cis, this being governed by the isomer ratio of the diol (CHDM) produced at the hydrogenation stage. The PCT does not crystallize as rapidly as PBT or nylon; its crystallization behavior is similar to that of PET and nucleants and plasticizers are often added to improve molding performance. The THERMX PCT comes in various glass-filled and FR grades. Typical properties of PCT are shown in Tables 10 and 11 (226). Table 10 shows the standard grades and Table 11 the FR grades.

## 20. PBT Molding Resins

Poly(butyleneterephthalate) is the oldest of the crystalline thermoplastic polyester molding resins, having been introduced by Celanese Corp. in 1970 under

Table 10. **Properties of THERMX PCT**[a]

| Polymer | CG011 | CG007 | CG041 |
|---|---|---|---|
| filler | 15% glass fiber | 30% glass fiber | 40% glass fiber |
| sp.gr. | 1.32 | 1.43 | 1.53 |
| tensile strength | 98 MPa:14,200 psi | 130 MPa:18,800 psi | 139 MPa:20,200 psi |
| elongation at break | 3.3% | 2.6% | 2.0% |
| flexural strength | 153 MPa:22,200 psi | 192 MPa:27,800 psi | 207 MPa:30,000 psi |
| flexural modulus | 4.9 GPa:0.71 Mpsi | 8.3 GPa: 1.2 Mpsi | 11.1 GPa: 1.61 Mpsi |
| notched Izod | 0.8 Ft·lb/in. | 1.4 Ft·lb/in. | 1.5 Ft·lb/in. |
| HDT at 264 psi | 245°C: 473°F | 263°C: 505°F | 265°C: 509°F |

[a] Standard grades.

Table 11. **Properties of THERMX PCT**[a]

| Polymer | CG912 | CG922 | CG932 | CG942 |
|---|---|---|---|---|
| filler | 15% glass | 20% glass | 30% glass | 40% glass |
| sp. gr. | 1.50 | 1.54 | 1.61 | 1.69 |
| tensile strength at break | 91 MPa<br>13,200 psi | 110 MPa<br>15,900 psi | 130 MPa<br>18,800 psi | 137 MPa<br>19,800 psi |
| elongation | 2.2% | 2.4% | 2.2% | 1.6% |
| flex strength | 142 MPa<br>21,000 psi | 162 MPa<br>23,200 psi | 184 MPa<br>26,700 psi | 203 MPa<br>29,000 psi |
| flex modulus | 5.1 GPa<br>0.74 Mpsi | 6.3 GPa<br>0.91 Mpsi | 8.6 GPa<br>1.25 Mpsi | 12.0 GPa<br>1.73 Mpsi |
| notched Izod | 0.9 ft·lb/in. | 1.1 ft·lb/in. | 1.4 ft·lb/in. | 1.4 ft·lb/in. |
| HDT at 264 psi | 224°C, 435°F | 239°C, 461°F | 241°C, 466°F | 251°C, 483°F |
| ULflammability | 94V-0 | 94V-0 | 94V-0 | 94V-0 |

[a] Flame retardant grades.

the trade name CELANEX (now marketed by Ticona). General Electric Co. then brought out their own version (VALOX) and today there are numerous suppliers including, BASF (ULTRADUR), Bayer AG (now Lanxess - POCAN), DuPont Plastics (CRASTIN), and DSM NV (ARNITE). Du Pont acquired Ciba-Geigy's PBT business in 1993 (227). In Japan, the major manufacturers are Polyplastics, Toray, Teijin, and Mitsubishi. As has been explained in the introductory section, PBT has the ability to crystallize as rapidly as nylon-6,6 in a cold mold to give tough, distortion-free moldings without additives or nucleating agents. While the unmodified polymer has very good flow properties, and is used in electrical connectors and fiber-optical cable buffer tubes, it performs even better if reinforced with inorganic fillers, notably chopped glass fiber, usually ~ 1/8 in. long. Additional mineral fillers are incorporated for special applications where stiffness and high heat deflection temperature are important. These mineral fillers include mica, talc, wollastonite and barium sulfate, the latter for special applications, eg, kitchen countertops.

The filled grades of PBT are tougher, stiffer, and stronger materials and they also have improved notched Izod impact strength, since unfilled PBT is notch-sensitive (228,229). Even when unfilled, the plastic has good strength, rigidity and toughness, low creep, minimal moisture absorbance, and does not undergo dimensional changes with changes in humidity. It is characterized by excellent electrical and dielectric properties and high surface finish. As a result, it has found wide acceptance in a variety of end uses, where precision molding and a high quality finish are required. Typical applications are in the electrical and electronic markets, where it is widely used in such parts as connectors, plugs, switches, typewriter and computer keyboard components, plug-in printed circuit boards, and small electric motor components. The PBT polymer is widely used in the automotive industry for electrical and ignition system components eg, distributor caps, bobbins, coil-formers, rotors, windshield wiper arms, headlight mountings, and other fittings. In the auto market, "under the hood" components have to maintain their dimensional stability at elevated temperatures, as well as being resistant to various automotive fluids. Other uses for PBT are home appliances, eg, food mixers, hair driers, coffee makers, toasters, and camera

Table 12. **Crystal Parameters for the Two Forms of PBT**[a]

| Parameter | α Form, unstretched | β Form, stretched |
|---|---|---|
| $a$, nm | 0.482 | 0.469 |
| $b$, nm | 0.593 | 0.580 |
| $c$, nm | 1.174 (1.165)* | 1.300 |
| α, deg | 100 (98.9)* | 102 |
| β, deg | 115.5 (116.6)* | 120.5 |
| γ, deg | 111 | 105 |
| density, g/cm$^3$ | 1.41 | 1.37 |

[a] See Ref. 232.

parts. Poly(butyleneterephthalate) is also used in industrial machinery, for example, in molded conveyor-belt links. An appreciable quantity is used in polymer alloys and blends with other polymers. This polymer is marketed in both standard and flame-retardant grades, the latter being essential to meet Underwriters' Laboratory 94V-0 standards in thin-walled sections. Glass-filled PBT is now a mature product; to sustain growth the tendency is for manufacturers and compounders to make more and more specialty grades with tailored properties to suit specific end-use demands.

## 21. Physical Properties of PBT

Unlike PET, the polymer PBT exists in two polymorphs called α and β forms, which have distinctly different crystal structures. The two forms are interconvertible under mechanical stress (230–232). Both crystal forms are triclinic and the crystal parameters are shown in Table 12.

The melting point of PBT is 222–224°C depending on the degree of crystallization and annealing conditions. The heat of fusion is ~ 140 J/g (233) and the $T_g$ is usually quoted at ~ 45°C, although this depends on the physical nature of the sample (234). The PBT polymer crystallizes so readily from the melt it is difficult to obtain a truly amorphous sample. Crystallization kinetics are not easy to determine (235). The density of the annealed crystalline unfilled polymer is 1.33 and 1.26 for the amorphous material (236). Like PET, PBT is made to various molecular weights, the $M_n$ values being in the 20,000–50,000 range. Intrinsic viscosities are usually measured in 2-chloro-phenol (OCP) or phenol–tetrachlorethane mixture. The Mark-Houwink parameters are shown in Table 13 (237,238).

Flame retardant recipes used in PBT–FR grades usually consist of synergistic mixtures of antimony trioxide with various brominated aromatic compounds. A typical recipe for PBT might be 10% w/w decabromodiphenyl oxide and 5% w/w antimony oxide. In recent years the trend has been to use polymeric or oligomeric

Table 13. **Mark-Houwink Parameters for PBT**

| Solvent | $K$ in dL/g | α |
|---|---|---|
| P/TCE, at 30°C | 1.17 × 10(−4) | 0.87 |
| OCP, at 25°C | 6.62 × 10(−5) | 0.915 |

brominated additives. A typical additive is an end-capped polycarbonate derived from tetrabromobisphenol-A [94334-64-2], while another is a mixture of epoxy oligomers derived from the diglycidyl ether of tetrabromobisphenol-A [68928-70-1]. Brominated polystyrenes (*loc. cit.*) have limited use in PBT as they have a poor compatibility (239). During the period 1993–1994, the market price of antimony metal and the trioxide rose very steeply. In fact the oxide tripled in price (240,241), which caused some FR-grade PBT producers and compounders seek cheaper formulations. During 1995, antimony trioxide prices partially retreated from their 1994 peak (242). As in other FR-grade polyesters, there is a pressure, notably in Europe, to eliminate brominated aromatic FR additives in favor of non-halogenated compounds, eg, phosphorus-based compounds. One interesting example is the use of red phosphorus as a FR agent in PBT and PET. As an additive it is inert until it burns, when it forms polyphosphoric acid with the other combustion products and acts as an intumescing agent which quenches the flame (243). Synergistic mixtures of phosphonate esters and melamine have been described as FR agents in PBT (244), but brominated FR recipes still dominate at the time of writing.

## 22. Chemical Properties

The PBT polymer is highly crystalline and like PET it does not suffer from solvent stress corrosion cracking, which is a constant problem with amorphous materials. It is resistant at room temperature to most common chemicals and solvents, lubricants, greases, and automotive fluids. Ketones will attack it at temperatures above ambient temperatures. Parts made from PBT are dishwasher safe, but will not withstand repeated steam autoclaving. The PBT is attacked by aqueous alkali and other strong bases and by dilute acids, particularly at elevated temperatures. It has very good resistance to weathering and black pigmented grades with uv-stabilizers have excellent outdoor stability. As with all polyesters, PBT is susceptible to hydrolytic attack by moisture in the melt. Injection molding screw temperatures are usually $\sim 250^\circ$C ($482^\circ$F) and IV drop will be very rapid unless the polymer chip is dried to $< 50$ ppm moisture content and *kept dry in the hopper*. Inadequate drying is probably the cause of more molding problems than any other single cause.

## 23. Mechanical Properties

Properties of typical grades of PBT, either as unfilled neat resin, glass-fiber filled and FR-grades are set out in Table 14. This table also includes impact-modified grades which incorporate dispersions of elastomeric particles inside the semicrystalline polyester matrix. These dispersions act as effective toughening agents that greatly improve impact properties. The mechanisms are not fully understood in all cases. The subject has been discussed in detail in a book by Bucknall (245) and the particular case of impact modified polyesters, eg, PBT, has been discussed in recent papers by Bucknall and co-workers (246) and by Hourston and co-workers (247).

Table 14. **Mechanical Properties of PBT**[a]

| Property | Unfilled grade[b] | 30%Glass GP[b] | 30%Glass FR[c] | 30%Glass HI[c] |
|---|---|---|---|---|
| spec. grav. | 1.31 | 1.54 | 1.66 | 1.53 |
| tensile strength | 8300 psi | 19,500 psi | 19,500 psi | 14,000 psi |
| tensile modulus | 0.360 Msi | 1.40 Msi | 1.7 Msi | 1.2 Msi |
| elongation | 5% | 2% | 1.5% | 3.1% |
| flexural strength | 12,400 psi | 28,000 psi | 28,000 psi | 22,000 psi |
| flexural modulus | 0.360 Msi | 1.2 Msi | 1.5 Msi | 1.0 Msi |
| notched Izod | 0.7 ft·lb/in. | 1.7 ft·lb/in. | 1.3 ft·lb/in. | 3.0 ft·lb/in. |
| unnotched Izod | 23 ft·lb/in. | 4.5 ft·lb/in. | 4.0 ft·lb/in. | 12 ft·lb/in. |
| HDT at 264 psi | 51°C, 123°F | 206°C, 403°F | 208°C, 406°F | 191°C, 376°F |
| volume resistv. | $10^{15}$ Ω·cm | $10^{16}$ Ω·cm | $5 \times 10^{15}$ Ω·cm | $4 \times 10^{14}$ Ω·cm |
| dielectric strength | 420 V/mil | 560 V/mil | 490 V/mil | 500 V/mil |
| dielectric const at 100 Hz | 3.2 | 3.7 | 3.9 | 4.3 |
| flammblty UL94 | HB at 1/32 in. | HB at 1/32 in. | V-0 at 1/32 in. | HB at 1/32 in. |

[a] See Ref. 248.

[b] Low molecular weight grade.

[c] General purpose = GP, flame retardant = FR, high impact = HI.

## 24. Processing

The PBT polymer is one of the easiest thermoplastics to injection mold provided the polymer is thoroughly dried before melting. The producers recommend 3–4 h at 121–138°C (250–280°F) predrying. Owing to its good flow properties and very high rate of crystallization in the mold, cycle times are short, making for high productivity. Typical molding conditions are shown in Table 15 for typical

Table 15. **Typical Injection-Molding Machine Settings for PBT Resin**

| | |
|---|---|
| melt temperature | 450–500°F for most grades, 430–480°F for FR grades<br>should not exceed 520°F for any grade. |
| mold temperature | 100–250°F, usually 100–200°F |
| injection pressure | 50–75% of maximum |
| injection speed | fast is preferred. Sometimes reduced in special cases |
| rpm | low-to-medium (fast enough to retract screw before mold opens |
| back pressure | low (0–50 psi) |
| cushion | 1/16 ft. to 1/8 in. recommended |
| cycle time | 5–45 s normal (depends on part thickness) |

glass-filled PBT resin. The melt temperatures may be reduced for FR grades, but the melt temperature should not exceed 270°C (520°F).

The PBT resins are very fluid in the melt and sometimes drooling from the injection nozzle can be a problem in machines that do not have melt decompression. A simple free-flow nozzle can be used satisfactorily to minimize drooling if its temperature can be adjusted by a separate heater band. PBT resins do not drool as badly as nylons.

## 25. Health and Safety Aspects

The PBT resins are not harmful or hazardous when handled at room temperature under normal conditions according to their Materials Safety Data Sheets. No problem with contact with the pellets has been encountered under normal conditions. Glass fines can however cause skin irritation, and if glass-filled resins are being ground or reground, due precautions must be taken. Inhalation of dust must be guarded against, as is true for grinding any glass-filled resin. During the molding the temperature must not exceed 520°F and never 550°F as decomposition with the evolution of harmful vapors can occur. As with all thermoplastics, adequate ventilation must be provided around injection molding machines, and so on.

## 26. Economic Aspects of PBT

The PBT polymer is a growing commercial thermoplastic. Back in 1993, the North American market (United States, Canada, and Mexico) for PBT was just > 200 million lb, a 15% increase over 1992 (249). The demand for all polyester resins in North America in 2003 was 600 million lb, of which 60% was PBT, giving a yearly PBT figure of 360 million lb. The overall polyester annual growth rate is estimated at 6%. Much more rapid growth of PBT demand is expected in the Asia Pacific region as molding facilities move offshore (250,251). This growth is accounted for mainly by two markets, electrical/electronic and automotive, which together accounted for well over half the PBT used. The major manufacturers of PBT in North America, Europe, and Japan are shown in the Table 16, but this does not include China, which will become a major factor.

Table 16. **Principal World Manufacturers of PBT According to Region**

| United States | Europe | Japan |
|---|---|---|
| General Electric | Bayer AG (Lanxess) | Polyplastics |
| Hoechst Celanese (Ticona) | BASF | Toray |
| DuPont | DuPont | General Electric |
| BASF | DSM NV | Mitsubishi Eng. Plastics |
|  | General Electric | Teijin |
|  |  | Toyobo |

Table 17. **Current United States Prices for PBT Resin Grades**

| Resin grade | > 1 m lb | 300,000–500,00 lb |
|---|---|---|
| PBT injection | 100–105 c/lb | 106–116 c/lb |
| PBT 30% glass FR | 133–143 c/lb | 143–153 c/lb |

In 2002 it was announced that Ticona and DSM would form a joint venture in the Netherlands to produce 60,000 tonnes /year PBT as well as the 60,000 tonnes/year Ticona plant at Shelby NC and the 30,000 tonne/year DSM plant at Emmen, The Netherlands. This new joint venture plant is planned to be on stream by the end of 2005. In the same article, it states that the world PBT capacity is 400,000 tonnes/year (252).

The future prospects for economic growth for PBT look good. It is still displacing thermosets, eg, phenolics and nylon and its versatility, excellent flow properties and ease of molding will assure it a prominent place in the thermoplastic world for many years to come. Current prices to date (Oct. 2005) are shown in the Table 17.

## 27. PTT Molding Resins

The PTT resin is a relative newcomer to the molding resin scene. It was first announced by Shell in July 1997 (253) under the name Corterra, which is the same as that of the Shell PTT fiber. It was claimed to combine the desirable properties of PET resins with the ease of processability of PBT, particularly its fast mold cycle times. The glass filled resin was stated to have outstanding strength, toughness and stiffness. Markets targeted were electrical/electronics, automobiles, appliances and furniture. Shell announced plans for a total PTT capacity of 200 million lb/year at a new plant in Geismar, Louisiana in 1999.

## 28. Physical Properties of PTT

One reason why PTT fiber has such outstanding resilience is its crystal structure, which features a pronounced zigzag chain (69) (Table 18). The two carbon–carbon bonds in the centre of the C3 diol unit are arranged in a gauche–gauche conformation. This may explain the ease of crystallization of PTT as a molding

Table 18. **Structure of PTT**[a,b]

| Parameter | Value |
|---|---|
| $a$, (nm) | 0.459 |
| $b$, (nm) | 0.621 |
| $c$, (nm) | 1.831 |
| $\alpha$, deg | 98 |
| $\beta$, deg | 90 |
| $\gamma$, deg | 112 |
| calculated crystal density | 1.441 g/cm$^3$ |

[a] *Source*: Ref. 331.

[b] See Refs. 68, 69, 254.

Table 19. **Mark-Houwink Factors for PTT**

| Solvent | Temperature, °C | $K$: $10^4$ dL/g | α |
|---|---|---|---|
| HFIP | 35 | 5.51 | 0.71 |
| 50/50 P/TCE | 30 | 8.2 | 0.63 |
| 60/40 P/TCE | 20 | 5.36 | 0.69 |

resin, since the polymer chains can readily adapt to the requisite conformation to allow maximum crystalline order to develop. The PBT polymer has a somewhat similar arrangement in which the three C–C bonds in the butanediol unit are arranged in a trans–gauche–trans conformation (255). The PTT crystallizes from the melt very rapidly and the highly crystalline polymer is not easily soluble. IVs have to be measured in solvents, eg, HFIP or phenol/tetrachlorethane.

Mark-Houwink parameters for three solvent systems are set out in Table 19 (256,257). The usual IV for melt spun PTT fibers is 0.80–0.92, which corresponds to $M_n$ values between 16,000 and 20,000 Da.

## 29. Mechanical Properties of PTT

Table 20 shows the main properties of PTT, both unfilled and glass filled

One of the unexpected properties of glass-filled PTT is the high stiffness (high flexural modulus), which allows parts to be molded with thinner sections. An example quoted (250,251) states that an automobile rocker-arm cover, made from 30% glass-filled PTT resin, needed a 0.15 in. wall thickness compared with a 0.18 in. wall for PBT to achieve the same stiffness. The use of PTT saved 14% in weight. A recent review of thermoplastic polyesters in the United States market notes that the Shell process for PDO (propane-1,3-diol) has now reduced its cost to ~$1.00/lb, making PTT resin competitive with both PET and PBT. A new 190 million lb/year continuous polymerization PTT plant in Montreal, Canada, is scheduled to commence production in 2005–2006. Most of the output will probably go into fiber end uses, but the resin market is not being neglected. A

Table 20. **Mechanical Properties of PTT Resin**[a]

| Property | Unreinforced | 30% Glass filled |
|---|---|---|
| tensile strength, psi (MPa) | 9802 (66) | 23,055 (155) |
| flexural modulus, psi (GPa) | 400,300 (2.67) | 1,501,100 (10.0) |
| HDT at 264 psi, °C (°F) | 59 (138) | 216 (421) |
| notched izod, ft·lb/in. | 0.9 | 2.0 |
| specific gravity, g/cm$^3$ | 1.35 | 1.55 |
| mold shrinkage, in./in. | 0.020 | 0.002 |
| melting point, °C (°F) | 225 (437) | |
| glass transition, °C (°F) | 45–75 (113–167) | |
| dielectric strength, v/mil | 530 | |
| dielectric constant, 1 MHz | 3.0 | |
| dissipation factor, 1 MHz | 0.015 | |
| volume resistivity, Ω·cm | $10^{15}$ | |

[a] See Refs. 250,251.

spokesman projects most nonfiber PTT will be used in polymer blends with polycarbonate, PET, or PBT. As molders and compounders become more familiar with PTT, some unexpected advantages have already shown up. Already it has been found that PTT molds to a very high component surface finish, and is more warp-resistant than other polyesters. It accepts pigments better than does PBT and less pigment is needed to give an equivalent color value. Compounders, such as RTP, in the United States and Epcos GmbH in Germany are working on flame-proof (V-0 rating) PTT compositions free from halogenated FR agents, goals that are difficult to meet with PBT (see previous section). The demand for PTT is necessarily small at the moment, but should blossom as supply eases and part manufacturers become more familiar with it.

## 30. Properties of PEN Polymer

To date, nobody is manufacturing PEN as a molding resin: apart from its use in blow molded containers (already covered), it is used mainly in fibers and films. The PEN has a more complex morphology than PET. When crystallized "cold" at temperatures $< 200°C$, it forms a triclinic crystalline phase with one chain per unit cell called the α-phase. If crystallized hot $> 200°C$, it forms a different triclinic phase with four chains per unit cell called the β-phase. The crystal parameters of both are set out in the Table 21 below. Like PET, the hot polymer may be quenched into an amorphous form which has a density of 1.325 g/cm$^3$.

## 31. Thermoplastic Copolyester Elastomers

Thermoplastic copolyester elastomers are generally block copolymers produced from short-chain aliphatic diols, aromatic diacids and polyalkylene ether-diols. They are often called polyesterether or polyester elastomers. The most significant commercial product is the copolymer from butane-1,4-diol, dimethyl terephthalate and polytetramethyleneether glycol [25190-06-1], which produces a segmented block copolyesterether with the structure shown below:

The polymer with the above structure has "hard" crystallizable segments of poly(tetramethyleneterephthalate), PBT, or 4GT (259–261). The "soft" segment phase is polytetramethylene ether glycol terephthalate, called PTMEG-T. The ratio of "soft" to "hard" segments determines the elastomeric nature of the copolymer. As

Table 21. **Crystal Parameters for the Two Forms of PEN**[a]

| Parameter | α PEN, triclinic | β PEN, triclinic |
|---|---|---|
| $a$ | 0.651 nm | 1.314 nm |
| $b$ | 0.575 | 0.904 |
| $c$ | 1.320 | 1.219 |
| α | 81.2° | 129.3° |
| β | 144 | 88.6 |
| γ | 100 | 90.8 |
| calculated density | 1.407 g/cm$^3$ | 1.436 g/cm$^3$ |

[a] See Ref. 258.

the percentage of soft segments increases, so does the elasticity of the copolymer. The 4GT hard segment imparts crystallinity, chemical, and thermal stability to the copolymer while the soft segment contributes toughness and elasticity.

Copolyesterether elastomers are considered to be high performance elastomers. In general, they are used in applications that involve some type of repeated mechanical movement, such as bending, flexing, pushing, rotating, pulsing, impacting, or recoiling. Such elastomers are used for one or all of the following reasons: (*1*) they have an excellent combination of strength, toughness, flexibility and recovery from deformation; (*2*) they have excellent chemical resistance; (*3*) they are capable of being used at high temperatures.

Several grades of such elastomers are supplied depending on the amount of PTMEG -T units in the final polymer. The polymers are classified as are other elastomers and rubbers of their Shore A or D hardness. The copolymers are generally available in hardnesses ranging from Shore D 35 to Shore D 82.

As with all thermoplastic elastomers the copolyesterethers can be processed as a thermoplastic. They are linear polymers and contain no chemical cross-links. Thus the vulcanization step needed for thermosetting elastomers is eliminated and scrap elastomer can be reused in the same process as virgin material. Several references to copolyester elastomers are listed in the bibliography (259–263).

## 32. Physical Properties and Morphology

Elastomers require some system of cross-bonding that links the flexible molecular chains to each other to give a stable network structure. Without this network, the elastomer would not have the properties to make it commercially useful. Thermoset elastomers accomplish this by forming molecular cross-links, irreversible chemical bonds formed during the vulcanization step. As previously stated, thermoplastic elastomers do need a vulcanization step and the network is produced by reversible physical bonds between the polymer chains (264). Copolyesterether elastomers are cross-bonded through a crystallization process. These block copolymers contain a crystalline phase that physically locks the flexible soft segments into an elastic network below the crystalline melting point of this phase.

In these structures, the crystalline 4GT units provide the ties to the soft amorphous regions (264) that are made up of both PTMEG-T and amorphous 4GT units. From a structural viewpoint, this crystallization of the 4GT units is a fundamental determinant of the attributes of the elastomer. Morphological studies of such copolymers suggest that the 4GT crystallites are dispersed within the soft amorphous regions. The properties are related to this two-phase morphology in the following statement (265): "*. . .the extent of hard segment/soft segment mixing will depend on overall hard segment content, both segment lengths and the affinity of one segment for the other. . .*"

Since the crystalline cross-links are reversible, the morphology and hence the utility of the elastomer is temperature dependent. Once the 4GT units have melted there is no more structure. This melting point depends on the percentage 4GT content in the copolymer. As the melt cools, the crystalline regions reform and the morphological structure reestablishes itself. The 4GT crystals grow, which then tie together the amorphous segments. There are in fact two

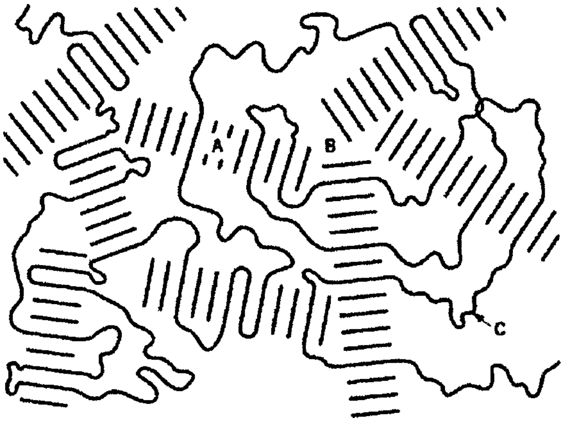


**Fig. 2.** Interpenetrating network morphology of thermoplastic elastomer where A = the crystalline domain, B = the junction of crystalline lamellae, and C = the noncrystalline 4GT segments (264).

models for the two-phase structure in the polyesterether elastomers. The first model (264) considers the structure to be that of an interpenetrating polymer network (see Fig. 2) in which it is suggested that "...*continuous and interpenetrating crystalline and amorphous regions exist where the randomly oriented and interconnected lamellar hard segments serve to anchor elastomeric portions of the molecule and thus provide physical cross-linking*..." (266). The second model due to Seymour and co-workers (267) considers a spherulitic structure (see Fig. 3)

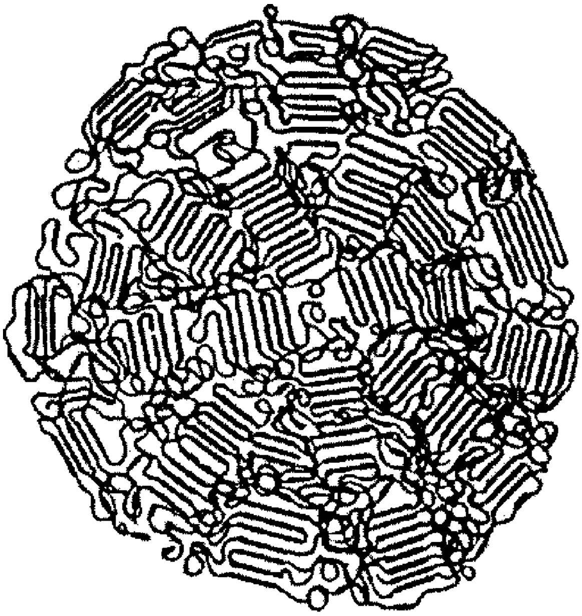


**Fig. 3.** Spherulitic morphology of thermoplastic elastomer where the heavy lines represent polyester segments (267).

consisting of "*...4GT radial lamellae with inter-radial amorphous regions which are a mixture of PTMEG-T soft segments and uncrystallized 4GT hard segments. ...*" In either case the crystallized 4GT segments provide a superstructure to tie together the amorphous 4GT and the PTMEG-T soft segments, with the latter two forming a single phase. Note that several papers have been published that provide evidence for an analogy between copolyesterether elastomer spherulitic morphology and semicrystalline thermoplastics and copolymers (266–271). Like semicrystalline copolymers, the 4GT polyesterether elastomers exhibit only one glass–rubber transition and one crystalline melting point temperature as measured by DSC or DMA.

Other morphological features of interest are

1. Increasing the concentration of the amorphous region decreases the melt temperature and lowers the $T_g$ to the same values as those of the PTMEG-T homopolymer (266).
2. There can be different states of order within the "amorphous" area. This is evidenced by a broadening of the glass transition peak (271).
3. Sample preparation will affects the details of the morphological characterization.
4. The chain conformation of 4GT-PTMEG-T elastomers was investigated by Miller and co-workers (272). They found that the PTMEG-T segments have a slightly expanded coil conformation while the 4GT segments exhibit a chain-folded structure.
5. Three types of long spacing were observed in X-ray scattering in samples studied with and without stress (273).
6. Scattering behavior or drawn annealed bristles was studied by small-angle X-ray scattering for the copolyesterether elastomer based upon 4GT and polyethylene glycol terephthalate (274).

Table 22 lists some of the characteristics of a series of 4GT-PTMEG-T elastomers.

## 33. Mechanical Properties

Commercial grades of copolyesterether elastomers generally range from Shore Hardness 35 to SH-82. These products are mechanically durable with high tensile

Table 22. **Polyesterether Elastomer Characterization**[a]

| 4GT cont. | 33% | 50% | 57% | 63% | 76% | 84% |
|---|---|---|---|---|---|---|
| 4GT block length, A | 2.64 | 4.95 | 6.43 | 8.14 | 14.8 | 24.26 |
| $T_m$,[b] | 163°C | 189°C | 196°C | 200°C | 209°C | 214°C |
| heat of fusion[b] | 3.9 cal/g | 7.8 cal/g | 9.8 cal/g | 11.4 cal/g | 13.9 cal/g | 14.6 cal/g |
| % Xllnity | 11.5 | 22.9 | 28.6 | 33.3 | 40.7 | 42.8 |
| E" peak deg C[c] | −63 | −58 | −53 | −48 | −30 | −4 |
| tan peak deg C[c] | −51 | −42 | −34 | −27 | + 10 | + 30 |

[a] See Ref. 266.
[b] From DSC.
[c] From DMA.

Table 23. **Selected Mechanical Properties of 4GT-PTMEG-T Elastomers**

| Properties | ASTM test | Units | 35D | 40D | 55D | 72D |
|---|---|---|---|---|---|---|
| durometer | D2240 | Shore D | 35 | 40 | 55 | 72 |
| sp. grav. | D792 | | 1.14 | 1.15 | 1.19 | 1.26 |
| tensile | D638, 5% | psi | 380 | 561 | 1291 | 2760 |
| strength | 10% | | 607 | 912 | 1884 | 3628 |
| type I | | | | | | |
| tensile strength type II | D638 (at break) | psi | 1920 | 3000 | 3650 | 4240 |
| elongation at break | D638 | % | 470 | 480 | 430 | 300 |
| flex mod | | | 12,300 | 22,400 | 98,200 | 343,700 |
| at −40°C | | | 8800 | 12,300 | 30,500 | 74,200 |
| at 23°C | D790 | psi | 4650 | 7500 | 16,100 | 32,200 |
| at 100°C | | | | | | |
| izod imp at −40°C | | | no break | no break | 2.7 | 0.7 |
| at 23°C | D256 | ft·lb/in. | no break | no break | no break | no break |
| tear strength | D1004 | lb/in. | 575 | 630 | 840 | 1240 |
| Tabor abrasion, H-18 1000 g | D1044 | mg/1000 cycles | 121 | 90 | 85 | 30 |
| melt point | D3418 | °C | 164 | 180 | 200 | 214 |
| Vicat temp | D1525 | °C | 107 | 136 | 181 | 204 |

strength and high load-bearing capabilities for an elastomer. They are very resilient, have low hysteresis and excellent creep resistance. In addition they have high tear strength, good abrasion resistance and a long flex life. Of special importance is the combination of high temperature properties coupled with very good chemical resistance. Table 23 shows the properties of selected grades of polyesterether elastomers (275). These grades are representative of major commercially available polyesterether elastomers. This table shows several key properties, notably Vicat Softening Point, Tear Strength, Flex Fatigue, stress/strain characteristics, low temperature properties and resistance to chemicals.

Polyester elastomers are resistant to a variety of common solvents including aqueous acids or bases. The chemical resistance of copolyesterether elastomers is shown in Table 24 (276) which gives examples of solvent resistance and is not inclusive.

Copolyesterether elastomers have excellent resistance to flex fatigue. For example, in the Ross Flex Test (ASTM D-1052), all of the above samples resisted cut-growth by $> 300{,}000$ cycles.

Typical stress–strain curves are shown in Fig. 4 (264). The stress/strain curve has three regions. At low strains, below $\sim 10\%$, these materials are considered to be essentially elastic. At strains up to 300%, orientation occurs that degrades the crystalline regions causing substantial permanent "set". At strains $> 300\%$ the stress occurs mostly in the amorphous regions up to the point where the sample breaks. All of the grades exhibit permanent set, and the curves of

Table 24. **Chemical Resistance of Polyesterether Elastomers**

| Chemical | Rating | Chemical | Rating[a] |
|---|---|---|---|
| acetone | G | mineral oil | E |
| ASTM Oil No. 1 | E | nitric acid 10% | G |
| ASTM Oil No. 3 | E | nitric acid >30% | NR |
| ASTM Ref Fuel A | E | SAE No. 10 oil | E |
| ASTM Ref Fuel C | E | sea water | E |
| ethanol | E | skydrol 500B | E |
| formic acid | G | soap solution | E |
| isopropyl alcohol | E | water (158°F) | G |
| methyl ethyl ketone | G (35-55D) | water (boiling) | E |
| methyl ethyl ketone | E (72-82D) | zinc chloride soln. | E |

[a] Rating Guide: E = No adverse reaction, little or no absorption, little or no effect on mechanical properties. G = Some effect, some absorption causing slight swelling, and reduction in mechanical properties. NR = Not recommended; material adversely affected in a short time.

grade with a Shore Hardness of 55 and higher exhibit a yield point. Special grades of elastomer are available to provide hydrolysis resistance (277), improved heat aging (278) and improved uv stability (279).

## 34. Manufacture

Polyesterether elastomers are made by a polycondensation reaction, either batchwise or by continuous polymerization processes. The reaction proceeds in two steps, the first stage being an ester interchange followed by a polycondensation step, exactly analogous to the steps used in the manufacture of PET or PBT. The manufacture generally proceeds in the following manner.

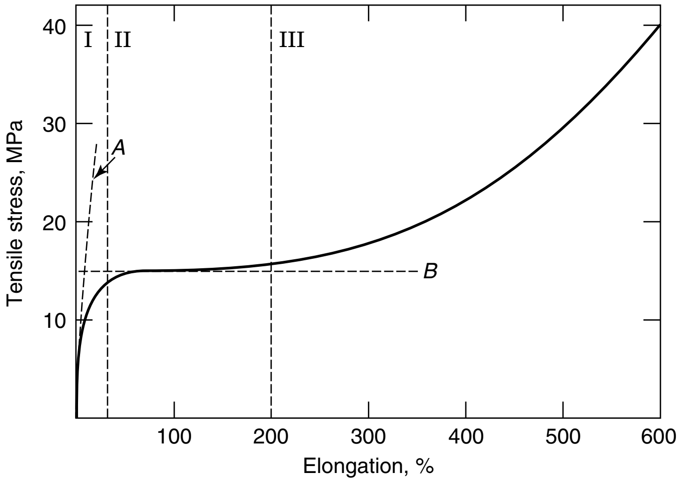


**Fig. 4.** Stress–strain curve of typical polyesterether elastomer showing the three main regions (I, II, and III) (264), where *A* is the slope (Young's modulus) and *B* is the yield stress. To convert MPa to psi, multiply by 145.

Dimethylterephthalate (DMT), polytetramethylene oxide diol (PTMEG) and excess of butane-1,4-diol are reacted in the presence of a titanium catalyst and the methanol evolved is distilled out of the reaction mixture (261). When the ester exchange is complete the reaction mixture is subjected to gradually diminished pressure to distil out the excess butanediol and drive the polymerization to completion, eventually under full vacuum. The batch temperature must be kept $< 250^\circ$C to avoid thermal degradation, and generally an antioxidant is added to protect the polyether segment from oxidative degradation. As the batch builds molecular weight, the melt-viscosity increases and the power consumed by the agitator motor is taken as a measure of the degree of polymerization. When the desired end point is reached, the vacuum is released with inert gas and the batch discharged under pressure through a die-plate into molten strands which are cooled in a water bath and chopped into pellets for drying and bagging. The distilled methanol and butane-diol can then be redistilled for recovery.

Other comonomers can be incorporated into at the polymerization stage and some typical ones that have been described are but-2-en-1,4-diol (280), dimethyl sebacate (259,261), dimethyl orthophthalate (259,261), dimethyl isophthalate (259,261), dimethyl *m*-terphenyl-4,4”-dicarboxylate (259,261) and the dimethyl ester of cyclohexane-1,4-dicarboxylic acid (270). In some cases, the butanediol is replaced partly or completely by other diols, eg, ethylene glycol (259,261) or cyclohexanedimethanol (281). Other polyether diols can be used in place of PTMEG. The most common are polyethylene glycol and polypropylene glycol, derived, respectively, from ethylene oxide and propylene oxide. Elastomers made from these polyether-diols have been compared (282). Elastomeric copolymers can also be made by replacing the PTMEG with a hydrocarbon soft segment such as those derived from dimer acids (283,284). The dimethylterephthalate can be replaced totally or partially by the dimethyl ester of NDA (285).

## 35. Processing

Injection molding is probably the most important process for shaping polyesterether elastomer parts. However, extrusion and blow molding are also important. All melt processing demands that the polymer pellets must be thoroughly dried before melt processing. The polymer has an equilibrium moisture content of 0.2% but this must be dried to $< 0.05\%$ if hydrolytic degradation is to be avoided. Recommended conditions for drying are 4 h at 105–110°C (263). Molding conditions depend on elastomer grade, but using the same grades as in Table 17, the conditions as set out in Table 25 are obtained.

Processing conditions for blow molding and extrusion will be somewhat similar to those for injection molding, but cooler temperatures are required to achieve higher viscosities for extrusion and blow molding. Thus the front end temperatures will be at the colder end of the above ranges. Other methods of fabrication are rotational molding, film extrusion and melt casting. The processing of polyesterether elastomers has been compared with the processing of other thermoplastic elastomers such as styrenics and urethanes (286).

Table 25. **Molding Conditions for Polyesterether Elastomers**

| Polymer | Grade | 35D (Shore) | 40D | 55D | 72D |
|---|---|---|---|---|---|
| rear barrel | temperature | 155–170°C | 162–182°C | 200–215°C | 200–215°C |
| mid-barrel | temperature | 170–182°C | 182–200°C | 215–232°C | 215–232°C |
| front barrel | temperature | 170–182°C | 182–205°C | 215–238°C | 215–238°C |
| nozzle | temperature | 170–188°C | 182–205°C | 215–238°C | 215–238°C |
| melt | temperature | 170–188°C | 182–205°C | 220–238°C | 220–238°C |
| mold | temperature | 25–52°C | 25–52°C | 25–52°C | 25–52°C |
| injection | pressure | low–medium | low–medium | low–medium | low–medium |
| injection | speed | fast | fast | fast | fast |
| screw | speed rpm | 60–125 | 60–125 | 60–125 | 60–125 |
| back | pressure | 0–50 psi | 0–50 | 0–50 | 0–50 |
| cushion/pad | mm | 5–10 | 5–10 | 5–10 | 5–10 |

## 36. Health and Safety Issues

Polyesterether elastomers derived from dimethyl terephthalate, butanediol and PTMEG are not hazardous according to the published Materials Safety Data Sheets (MSDS) for this elastomer. Polymers of a similar structure containing isophthalic acid are also not considered hazardous. For other copolymer elastomers, the MSDSs put out by the suppliers should be consulted by potential users before evaluation. One environmental advantage of thermoplastic elastomers of this type is that they are melt-reprocessable and thus scrap and off-specification material and even obsolete parts can be easily recycled. Up to 25% by weight of recycled material can be incorporated.

## 37. Uses

The market for polyesterether elastomers was expected to grow to 125 million lb by 1996 (287). A projected world market situation is shown in Table 26.

The major market segments for thermoplastic elastomers in 1987 were reported (287) to have the various market shares as shown in Table 27.

Table 26. **Polyesterether Elastomer World Market**[a]

| Region | 1996 Projection, lb | Growth rate 1986–1996, % |
|---|---|---|
| United States | 75,000,000 | 10.1 |
| Western Europe | 30,000,000 | 11.6 |
| Japan | 29,000,000 | 14.0 |

[a] See Ref. 287.

Table 27. **Market Share of Polyesterether Elastomers in 1987**[a]

| Market | United States, % | Western Europe, % | Japan, % |
|---|---|---|---|
| wire and cable | 13 | 10 | 11 |
| automotive | 13 | 25 | 44 |
| footware | 4 | 12 | |
| hose and tubing | 13 | 14 | 11 |
| other industrial | 57 | 39 | 34 |

[a] See Ref. 288.

Specific applications for polyesterether elastomers are too numerous to mention in detail, but a list of applications with references where appropriate is shown in Table 28. This is by no means complete, but is merely representative of the vast range of potential applications.

## 38. Manufacturers

The main suppliers of polyesterether elastomers and the trade names of their products are shown in Table 29. Among the end-uses for these elastomers, an important one is in blends with PBT to make polymer alloys such as VANDAR or BEXLOY. These alloys are very tough and find uses in such applications as automobile fascias (293), wheel covers, and air-bag housings.

## 39. Liquid-Crystal Polymers: Background

Most crystalline substances undergo a single transition from a solid state to an isotropic liquid phase. However, some molecules, both small molecules and polymers, can exist in an ordered liquid phase or *mesophase*. Such substances are called *liquid crystals*. The mesophase state is intermediate between a structured solid and an isotropic or disordered liquid. A striking manifestation of this structure is that a liquid-crystal melt is often birefringent between crossed polarizers

Table 28. **List of Applications**[a]

hydraulic hosing (263)
release binders (263)
door lock bumpers (289)
headphones (290)
jacketing (290)
diaphragms for railroad cars (260)
railroad draft gear (260)
CVJ boots (291)
conductive rubbers (292)
energy management devices (291)
compression spring pads (290)
gun holsters (260)
run-flat tire inserts (291)
rail car couplers (288)
auto vacuum control tubing
railroad car shock absorbers (260)
specialty fibers, films, and sheets
automotive shock absorbers
corrugated plasic tubing
auto electric window drive tapes
recreational footware
wire coatings (263)
telephone handset cords (289)
wire clamps (291)
drive belts (260)
medical films (283)

[a] References are in parenthesis.

Table 29. **Revised List of Manufacturers and Trade Names of Polyesterether Elastomers**

| | |
|---|---|
| Du Pont | HYTREL |
| General Electric | LoMod (discontinued since 1999)[a] |
| Hoechst Celanese (now Ticona) | RITEFLEX (VANDAR - alloy) |
| Eastman | ECDEL |
| DSM | ARNITEL |

[a] On Feb. 23, 1999 GE announced that LoMod would cease production and customers would be supplied from DSM with Arnitel.

in the polarizing hot-stage microscope and displays vivid colors when sheared. There are many types of mesophase, but they all fall into two main categories; those that possess some measure of 3D order and those that have only rotational (1D) order and that are therefore fluid. It is this dual property of behaving like a liquid and a solid that gives rise to many interesting properties.

Most polymeric liquid crystals are based upon stiff rod-like molecular units that are called *calamitic* mesogens. There are some unusual polymers, not discussed here, that contain flat disk-like molecular units called *discotic* mesogens in which the disks form columnar arrays like stacks of poker chips. Another major distinction is that between mesophases that exist only in solution and are called *lyotropic mesophases* and those that can exist by altering the temperature. These are called *thermotropic mesophases*. Lyotropic mesophases typically form from solutions of stiff rod-like polymers in solvents above a certain critical concentration (294) and an excellent example is the polyamide KEVLAR, which was first commercialized in the 1960s by Du Pont. Other examples are certain peptides, eg, poly ($\gamma$-benzyl-L-glutamate) and proteins such as tobacco mosaic virus. Liquid crystals can also be classified, according to their molecular symmetry, as *nematic, cholesteric*, and *smectic*. Nematic liquid crystals have long-range orientational order and the molecules tend to align themselves parallel to each other, but there is no long-range correlation of molecular position. Cholesteric mesophase order is only found in chiral nematic molecules and here layers or sheets of nematic order exist, but superimposed upon this is a spiral ordering like a twisted deck of cards. The smectic order is the most complex and many smectic states exist. It is also possible to have chiral smectic states. All are characterized by both orientational and positional order to varying degrees. Two common smectic types are smectic A, where the mesogens are orthogonal and have end-register positional order, and smectic C, which is similar, except that the mesogens are all tilted. Due to the positional order of smectic phases they are much more viscous than nematic polymers. An interesting anecdote concerns some unpublished work done at ICI Fibers Division in Harrogate, the United Kingdom, during 1959–1961 concerning the polyester from 4, 4′-bibenzoic acid and hexane-1, 6-diol. Despite much effort, this material could not be melt-spun into fibers. Its behavior baffled researchers at the time. Although its melting point was well below its decomposition point, no coherent molten threadline could be maintained and the extrudate flew off the windup as short, brittle, crystalline lengths. The spinning pressure was puzzling as it was inordinately high for the polymer IV. Not until many years later did other workers demonstrate that this polymer, on cooling from the molten state, exhibits a mesophase transition directly from an isotropic melt to a smectic-A phase. Good sources of information on liquid crystals and liquid-crystal polymers are the books by Priestley and co-workers (295), Carfagna (296) and the articles by Dobb and McIntyre (297), Calundann and Jaffe (298) and Chung and co-workers (299).

Polymers have been described exhibiting all types of mesophase character, but the only ones to have practical commercial utility as structural materials are rod-like polymers that exist in nematic mesophases. As previously explained in the introductory section, these polymers are aromatic polyesters (or polyesteramides) that frequently contain units derived from 4-hydroxybenzoic acid. The literature on liquid-crystal polyesters is now voluminous: A selection of relevant publications will be found in the bibliography. The abbreviation LCP will hereafter refer to thermotropic liquid-crystalline aromatic polyesters. The history and outline polymerization chemistry of LCPs has already been discussed. In commercial terms, Dartco licensed the Carborundum technology and built a plant in the United States to manufacture XYDAR for Tupperware. This plant was sold to Amoco in 1987. Meanwhile Celanese Corporation had introduced its VECTRA range of LCP resins as an advanced engineering plastic in 1985 and a new plant was built at Shelby in North Carolina. DuPont, after several false starts, began to produce their own ZENITE range in the United States in the 1990s. In Japan, Sumitomo, Unitika, and Polyplastics in Japan have made commercial LCPs while in Europe ICI first began, then abandoned, their own LCP product. Both BASF and Bayer AG also began to produce commercial material, but at the time of writing, the LCP market is dominated by Celanese (now Ticona) and Amoco (now Solvay) and Du Pont Plastics products.

## 40. Molecular Structure of LCPs

At present, there are no rigorous criteria for predicting the liquid-crystal nature of any polymeric structure, but some generalizations can be made. First, the persistence length of LCPs is greater by a factor of 2 or 3 times than that of random-coil polymers. Generally, lyotropic polymers have a greater persistence length than thermotropic polymers. According to Flory, an axial ratio of 6.42 is required for a polymer to be stiff enough to form a thermotropic melt (300–302). Chain stiffness and interaction between the neighboring chains are the key parameters that will determine whether or not a polymer will form a mesophase. Most LCPs have a large polarizability along the rigid chain axis compared to that in a transverse direction. 4-Hydroxy-benzoic acid, HBA, is a key ingredient in the majority of commerical LCPs. When copolymerized into polyester structures, it imparts the correct amount of polymer chain stiffness and degree of interaction to lead to the formation of a mesophase state. It is also available and reasonably inexpensive. The homopolymer has an exceedingly high melting transition (Cottis and Economy, *loc. cit.*) and copolymers are made to lower the solid-nematic transition (melting point) to make the polymer tractable and useful. The polymer chemistry will be discussed a little later.

During thermoplastic processing (eg, extrusion or injection molding) the polymer flows in the liquid-crystal (nematic) phase. The relatively rigid rod-like polymer chains align themselves in the flow direction and there is little or no entanglement, giving a very fluid melt. As a result, such polymers are ideally suited to molding intricate and finely detailed components. After cooling the aligned chains are frozen with some net alignment remaining in the flow direction. This is called the frozen-liquid crystal state. Due to this orientation effect, LCPs typically exhibit anisotropic properties.

## 41. LCPs as Molding Resins

The LCPs are in many ways materials ideally suited for injection molding. Their balance of properties is particularly well suited to the electrical connector and electronics industries. Some of the principal advantages of LCPs as molding resins follow:

1. Extremely low shrinkage and warpage and exceptional dimensional stability.
2. High melt strength for ease of fabrication.
3. Low melt viscosity at high flow rates in thin sections and in intricate molds.
4. Low heat of fusion for very fast cooling and short cycle times.
5. Low flash due to low injection pressures and shear-sensitive viscosity.
6. High stiffness at high temperatures allows parts to be hot-ejected without distortion.

In addition, LCPs offer, by their virtue of their chemical nature as all-aromatic crystalline polyesters, a combination of physical and chemical properties that no other single class of polymers can demonstrate:

1. Excellent thermal stability: UL relative thermal index up to 240°C, depending on grade of LCP.
2. High rigidity and strength; typical values are modulus 10–24 GPa (1.4–3.5 Msi), tensile strength 125–225 MPa (18–37 Ksi), and notched Izod values from 1.1–7.5 J (1.6–5.5 ft·lb/in.).
3. Retain 70% impact value even down to 4 K. (Most other plastics are extremely brittle at cryogenic temperatures.)
4. Inert to a wide range of chemical agents, acids, bleaches, chlorinated solvents, fuels, alcohols.
5. High barrier properties and very low permeation rates due to close-knit molecular structure.
6. Very low level of ionic contamination, well below those needed for corrosion-free environments in electronic integrated circuitry.
7. Inherently flame retardant, low smoke density, and combustion products are relatively nontoxic.
8. Regrind polymer maintains nearly all properties of virgin resin.

## 42. Typical Commercial LCPs: Synthesis and Properties

The outline of LCP synthesis has already been discussed: nearly all are made by the acidolysis route. The *in situ* acetylation polymerization route that starts from the free hydroxy compounds and carboxylic acids rather than preformed acetylated monomers is increasingly used as larger polymer batches can be made in the same reactor vessel. Polymerizations can be run batchwise or continuously and the volatile acetic acid is removed by distillation under vacuum in the conventional way. Because of the corrosive nature of this by-product, the reactors must be made of a corrosion resistant alloy. Stainless steel is generally adequate but some manufacturers prefer to use Hastelloy. Several unique problems arise in LCP polymerization due to the extreme shear sensitivity of the LCP melt. One is agitator design: the problem of toffee-appling has already been mentioned. Incidentally, in the mesophase nematic state the polymer melt is opaque, unlike the clear melt of a normal isotropic polymer (303,304).

For very high melting polymers, sometimes a slurry or nonaqueous dispersion polymerization (NAD) route is used. In this case, the reaction is run in a high boiling inert solvent as a reaction medium. The starting materials are usually soluble at the commencement, but as the acetic acid distils out and the polymer molecular weight grows, the product separates out as a slurry or dispersion of fine particles, hence the name. The low molecular weight prepolymers initially formed presumably undergo a form of solid-state polymerization in the later stages of the process. This method enables high melting polymers to be made under more normal conditions and produces the polymer in a finely divided powder form. The disadvantages are (*1*) the presence of the inert solvent reduces the size of the polymer batch; (*2*) the product usually has to be solvent washed to remove and recover the inert reaction medium. Both of these factors add to the process cost. However, the technique has been described in the patent literature several times (305,306).

The three major commercial LCPs polymers are VECTRA, XYDAR, and ZENITE. All are based on 4-hydroxybenzoic acid, which is copolymerized with 6-hydroxy-2-naphthoic acid in the case of VECTRA (25) and with a mixture of 4,4'-biphenol and terephthalic acid (some compositions are believed to also include isophthalic acid) in the case of XYDAR (307). Both types of copolymers lead to lower melting points, but the $T_\mathrm{m}$ of XYDAR is $\sim 420°\mathrm{C}$ (790°F), which is considerably above that of most thermoplastic polyesters. This gives XYDAR outstanding high temperature performance at the cost of some added difficulties during processing. VECTRA comes in various grades and compositions (308–311). Some of these grades are intended for high temperature end uses. The VECTRA-A polymer melts at 280°C (535°F), which is much more in the range of normal processing conditions. The VECTRA-B series of resins is particularly suitable for the extrusion market. This polymer is a polyester-amide (81,312–315) and has exceptional stiffness and high modulus. This appears to be due to a favorable molecular alignment brought on during elongational flow during extrusion, which is more effective for this composition than for normal LCPs (316,317). VECTRA-B resins have a melting point very close to that of the VECTRA-A series.

Du Pont's ZENITE range of LCPs have been reintroduced. These materials are LCP polyesters based upon HBA copolymers with various amounts of 4,4′-biphenol, terephthalic acid, and naphthalene-2,6-dicarboxylic acid (NDA) as comonomers. Their compositions are thus similar to those of XYDAR with added NDA to further reduce the melting point (318,319).

## 43. Injection Molding LCPs

The VECTRA range of LCPs comprise the leading commercial materials for injection molding. The high degree of molecular alignment in the flow direction during the molding process gives the finished part an anisotropic quality; the part is stronger in the direction of flow than across it, a phenomenon observed by Jackson and Kuhfuss in the very early days of LCP technology (18). Owing to this molecular alignment, the shrinkage properties are very low or zero in the direction of alignment, but across the flow direction, the shrinkage is close to that of a normal isotropic polymer. Typically, along the flow direction the shrinkage is 0.00–0.001 in./in., and across the flow 0.05 in./in.

The LCPs are remarkable for combinations of properties unmatched by any other thermoplastic. They have low melt viscosity, low flash, high heat resistance, and high dimensional stability. The rigid (or semirigid) rod-like nature of the polymer chains in LCPs results in a profile of molecular orientation that resembles the physical orientation of fibers in a fiber-reinforced thermoplastic. During injection molding the skin is oriented in the flow direction and may comprise 15–30% of the thickness of the total part. Generally, as the section becomes thinner, the proportion of skin increases. The skin has high strength and modulus and good tensile performance, but the very high level of orientation can cause the surface of unfilled parts to fibrillate or peel off as fine fibers under abrasion. This is prevented by filling the polymer with an inorganic filler, eg, glass, wollastonite. Typically, LCPs are sold as glass-filled compounded resins. As the percentage of glass increases the stiffness and strength go up, while impact properties, eg, notched Izod values come down. HDT also increases with glass content and the degree of anisotropy decreases in the final molded part.

Weld-line effects are common to all injection moldings where two polymer melt fronts meet as in multiple gate molds. This effect is particularly noticeable in the case of LCPs due the highly anisotropic liquid-crystalline nature of the melt and the domain microstructures associated with it. Because of these, the two melt fronts do not readily interpenetrate and the final molding has poor weld-line strength (320). This problem can be partially solved by using glass-filled resins, but the manufacturers recommend that weld-line problems be allowed for during the initial mold design and gates be positioned accordingly.

## 44. Properties of Typical Commercial LCPs

Table 30 sets out published (321) data of three major commercially available LCPs. Further details can be obtained from the manufacturers' published data sheets or are available over the Internet.

## 45. Rheology of Liquid-Crystal Polymers

Most conventional thermoplastics show evidence of shear thinning at high shear rates (1000 reciprocal seconds or more). The LCPs show evidence of shear thinning at much lower shear rates (18,322–324). Typically, low injection pressures

Table 30. **Mechanical Properties of LCPs**[a]

| Resin | Filler[b] | Density, g/cm$^3$ | Tensile, Kpsi | Elongn, % | Flx Mod, Msi | Notched Izod, ft·lb/in. | HDT at 264 psi |
|---|---|---|---|---|---|---|---|
| Vectra A950 | none | 1.4 | | | 1.3 | 10 | 356°F<br>180°C |
| Vectra A130 | 30% CG | 1.61 | 30 | | 2.1 | 2.8 | 446°F<br>230°C |
| Vectra A150 | 50% CG | 1.79 | 26 | | 2.9 | 1.7 | 449°F<br>232°C |
| Vectra A410 | 50% GF/MIN | 1.24 | 24.5 | | 2.7 | 1.6 | 536°F<br>280°C |
| Vectra B950 | none | 1.4 | 27 | | 2.2 | 8 | 392°F<br>200°C |
| Vectra C130 | 30% CG | 1.61 | 22 | | 1.9 | 2.4 | 465°F<br>240°C |
| Vectra C150 | 50% CG | 1.79 | 24 | | 2.8 | 1.6 | 485°F<br>252°C |
| ZENITE 6130 | 30% CG | 1.61 | 21 | | 1.8 | 2.6 | 482°F<br>250°C |
| ZENITE 7130 | 30% CG | 1.61 | 21 | | 1.9 | 2.6 | 535°F<br>279°C |
| HX- 2000 | none | 1.27 | 17 | 0.6 | 2.6 | 3.7 | 365°F<br>185°C |
| XYDAR G-930 | 30% GF | 1.6 | 19.6 | 1.6 | 1.95 | 11 | 520°F<br>271°C |
| XYDAR G-540 | 40% GF | 1.7 | 21.2 | 1.5 | 2.28 | | 466°F<br>241°C |

[a] *Note: Every sample has a UL 94 rating of V-0.*

[b] Chopped glass = CG, glass fiber = GF, mineral filler = MIN.

are needed in LCP molding compared with those for conventional thermoplastics. An excellent overview of the rheology of LCPs was published in 1990 by Dealy and Wissbrun (325). The long relaxation times of molten LCPs result in very low die-swell. It was demonstrated by Y Ide that significantly improved tensile properties resulted from extrusion through a die with either zero "land" (ie, the length of the cylindrical part of the hole) or very minimal land length (326). Injection-molded LCP parts have a distinct fibrous morphology that can only be obtained in an extensional flow process. Key processing and property advantages of LCPs in injection molding are the ability to fill long flow paths, thin walls, multiple cavities and multiple inserts, fast mold cycles, reduced injection and clamp pressures, low shrinkage and warpage and low thermal expansion coefficients in the machine direction due to the orientation of the molecules.

## 46. Chemical Resistance of LCPs

Liquid-crystal polymers in general are innately very resistant chemically to a variety of aggressive chemicals and solvents, due to their tightly packed highly

Table 31. **Chemical Resistance of VECTRA after 30 Day Exposure**

| Agent | Temperature, °F | Rating[a] |
|---|---|---|
| 80% formic acid | 216 | A |
| 70% chromic acid | 190 | B |
| 37% hydrochloric acid | 190 | A |
| 70% nitric acid | 190 | B |
| 10% caustic soda | 190 | A |
| 30% caustic soda | 190 | C |
| acetone | 133 | A |
| methylene chloride | 148 | A |
| ethyl acetate | 171 | A |
| gasoline | 250 | A |
| methanol fuel | 250 | B |
| skydrol | 160 | A |

[a] Essentially no effect = A, some change = B, not recommended = C.

aromatic molecular structure. Table 31 shows the stability of Vectra test-bars to various chemical agents (327).

## 47. Applications of Liquid-Crystal Polymers

The LCPs are almost ideal materials for injection molding compounds for electrical interconnect devices (328). In the electrical and electronics area, surface mount components (*loc.cit.*), connectors, chip carriers, ceramic replacements, bobbins, electric motor insulation, fiber optic components, closures and fuseholders are some of their applications. Other applications are bearings, bushings, gears, cams, microwave components, under-the-hood automotive components (including fuel systems, electronic and electrical systems), aerospace applications and aircraft components, including secondary structures, interior components for passenger aircraft, mechanical linkages, and other structural components. In other fields, applications exist in biomedical devices, printed circuit boards, pump, valves etc. The ease of fabrication and ability to replace complex assembly and machining operations with a single molded monolithic component, which may well perform more reliably than a built-up part, is particularly advantageous for LCPs given their great chemical resistance and excellent electrical properties. An article by A Kaslusky succinctly covers the whole applications area for LCPs (329) while another useful review of commercial LCP materials in general is that by English (330).

## 48. LCP Economics

The LCPs are expensive materials. Resin prices to date (October 2005) are shown in the Table 32 (331). Comparing the current figures with 1995 prices (332) the actual price has fallen by $\sim$ \$1.00 /lb for all grades, more if allowing for inflation.

One of the basic reasons for the high price is the cost of monomers and intermediates, a consequence of low volume, but the decline in actual (as well

Table 32. **Current Prices for LCP Resins**[a]

| | |
|---|---|
| LCP injection, glass filled | 610–980 c/lb |
| LCP injection mineral filled | 550–810 c/lb |
| LCP extrusion grade | 945–1180 c/lb |

[a] *Source*: Ref. 331.

as inflation adjusted) prices over the period 1995–2005 shows that as volume increases, prices have indeed fallen. The exact size of the world LCP market is difficult to determine from the open literature. It is a highly fragmented and specialized area and both suppliers and customers closely protect their proprietary sales information. A rough estimate of total world sales, based on a compounded resin basis, would be ~ 15–20 million lb/annum and in view of the close association with the electrical/electronics industry, a significant area of this business is in the Far East. The LCP market has been in existence for fifteen years and only relatively recently has it begun to make a major impact. However, the future looks to be bright for materials which offer so many combined property advantages wherever the specialized end-use justifies the price. At the time of going to press, Ticona have announced a 40% expansion of their VECTRA production capacity to take advantage of the withdrawal by Dow Chemical of their QUESTRA syndiotactic polystyrene (333).

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## BIBLIOGRAPHY

"Polyesters, Thermoplastic" in *ECT* 3rd ed., Vol. 18, pp. 549–574, by D. B. G. Jaquiss, W. F. H. Borman, and R. W. Campbell, General Electric Co.; in *ECT* 4th ed., Vol. 19, pp. 609–653, by A. J. East and M. Golden, Hoechst Celanese Corp., and S. Makhija, Consultant; "Polyesters, Thermoplastic" in *ECT* (online), posting date: December 4, 2000; by A. J. East and M. Golden, Hoechst Celanese Corp., and S. Makhija, Consultant.

## CITED PUBLICATIONS

1. I. Goodman, Polyesters, *Encyclopedia of Polymer Science & Engineering*, Vol. 12, John Wiley & Sons, Inc., New York, 1988, pp. 1–75.
2. H. Mark and G. S. Whitby, eds., *The Collected Works of W H Carothers on High Polymeric Substances*, Interscience Publishers, Inc., New York, 1940.
3. U.K. Pat. 578,079 (June 14, 1946), J. Rex Whinfield and J. T. Dickson (to ICI Ltd.).
4. U.S. Pat. 2,465,319 (March 22, 1949), Whinfield and Dickson (to E. I. du Pont de Nemours & Co., Inc.).
5. E. V. Martin and C. J. Kibler, *Science and Technology of Man-Made Fibers*, Vol. 3, in H. F. Mark, S. M. Atlas, E. Cernia, eds., New York, 1967.
6. *Mod. Plast. Int.* **20**(4), 8–10 (April 1990).
7. P. A. Aspy and E. E. Denison, *Mod. Plastics*, 74–76 (Aug. 1983).

8. U.K. Pat. 1,239,751 (July 21, 1971), A. J. Dijkstra, J. A. W. Reid, and I. Goodman (to ICI Ltd.).
9. U.S. Pat. 4,393,178 (July 12, 1983), R. M. H. Legras and co-workers (to Imperial Chemical Industries plc).
10. U.S. Pat. 4,380,621 (April 19, 1983), E. Nield, D. E. Higgins and M. W. Young (to Imperial Chemical Industries plc).
11. S. Beury, Chemical Market Associates Inc., *2006 World Terephthalates and Polyester Analysis*, August 31, 2005, see: http://www.cmaiglobal.com.
12. J. G. Cook, H. P. W. Hugill, and A. R. Low, Br. Pat. 604,073 (1948).
13. *Plastics Technol.* 55 (May 1995).
14. Celanese Corporation, unpublished work.
15. Ger. Offen. 2,052,971 (Dec. 3, 1970), S. Cottis, J. Economy, and B. E. Nowak (to Carborundum Corp.).
16. U.S. Pat. 3,829,406 (Oct. 1, 1971), S. Cottis, J. Economy, and B. E. Nowak (to Carborunum Corp.).
17. Ger. Offen. 2,507,066 (Sept. 2, 1976), S. Cottis, J. Economy, and L. C. Wohrere (to Carborundum Corp.).
18. W. J. Jackson and H. F. Kuhfuss, *J. Polym. Sci. Polym. Chem.* **14**, 2043–2058 (1976).
19. U.S. Pat. 4,181,792 (Jan. 1, 1980), W. J. Jackson and J. C. Morris (to Eastman Kodak Co.).
20. U.S. Pat. 3,991,013 (Nov. 9, 1976), T. C. Pletcher (to E. I. du Pont de Nemours & Co., Inc.).
21. U.S. Pat. 3,991,014 (Nov. 9, 1976), J. J. Kleinschuster (to E. I. du Pont de Nemours & Co., Inc.).
22. U.S. Pat. 4,066,620 (Jan. 3, 1978), T. C. Pletcher and J. J. Kleinschuster (to E. I. du Pont de Nemours & Co., Inc.).
23. U.S. Pat. 4,118,372 (Oct. 3, 1978), J. R. Schaefgen (to E. I. du Pont de Nemours & Co., Inc.).
24. U.K. Pat. 993,272 (May 26, 1965), I. Goodman, J. E. McIntyre, and D. H. Aldred (to ICI Ltd.).
25. U.S. Pat. 4,161,470 (July 17, 1979), G. W. Calundann (to Celanese Corp.).
26. W. S. Witts, *Chem. Proc. Eng.* **51**, 55 (1970).
27. U.S. Pat. 3,467,724 (Sept. 16, 1969), S. A. Laurich (to Chevron Research Co.).
28. U.S. Pat. 3,636,180 (Jan. 18, 1972), D. B. Broughton (to Universal Oil Products Co.).
29. U.K. Pat. 994,769 (June 10, 1965) (to Standard Oil Co.).
30. U.S. Pat. 3,584,039 (June 8, 1971), D. H. Meyer (to Standard Oil Co.).
31. J. Milgrom, Outlook for Plastics Recycling in the United States, Decision Resources Inc., 1993, pp. 25–27.
32. K. A. Domeshek, "Polyester Recycling: An Environmental Success Story" in *Tomorrow's Ideas and Profits: Polyester: Fifty Years of Achievement*, D. Brunnschweiler and J. Hearle, eds., The Textile Institute, Manchester, England, 1993, pp. 288–290.
33. U.S. Pat. 5,008,479 (April 16, 1991), Abe and co-workers (to Mitsubishi Gas Chemical Co.).
34. U.S. Pat. 5,276,230 (Jan. 4, 1994), Inamasa, Fushimi, and Takagawa (to Mitsubishi G. C. Co.).
35. U.S. Pat. 5,321,178 (June 14, 1994), Inamasa, Fushimi, and Takagawa (to Mitsubishi G. C. Co.).
36. U.S. Pat. 5,254,769 (Oct. 19, 1993), Takagawa, Yamagishi, and Nagagata (to Mitsubishi G. C. Co.).
37. U.S. Pat. 5,183,933 (Feb. 2, 1993), Harper and co-workers (to Amoco Corp.).
38. U.S. Pat. 5,169,977 (Dec. 8, 1992), Tanaka and co-workers (to Mitsubishi Gas Chemical Co.).

39. U.S. Pat. 5,254,719 (Oct. 19, 1993), Holzhauer and Young (to Amoco Corp.).
40. U.S. Pat. 5,262,560 (Nov. 16, 1993), Holzhauer and co-workers (to Amoco Corp.).
41. U.S. Pat. 5,256,817 (Oct. 26, 1993), Sikkenga and Hoover (to Amoco Corp.).
42. U.S. Pat. 6,072,098 (June 6, 2000), Takagawa and Shigematsu (to Mitsubishi Gas Chemical Co.).
43. U.S. Pat. 6,268,528 (July 31, 2001), Machida and co-workers (to Mitsubishi Gas Chemical Co.).
44. U.S. Pat. 5,523,473 (June 4, 1996), Saitou and co-workers (to Nippon Shokubi Co. Ltd.).
45. U.S. Pat. 6,833,472 (Dec. 21, 2004), Codignola (to Eurotecnica Development and Licensing SpA).
46. G. O. Curme and F. Johnston, "Glycols", in ACE Monograph No. 114, Rheinhold Publishing Corp., New York, 1952, Chapt. 2.
47. U.S. Pat. 3,920,759 (Nov. 18, 1975), E. V. Hort (to GAF Corp.).
48. U.S. Pat. 3,950,441 (April 13, 1976), S. Rudolf and W. DeThomas (to GAF Corp.).
49. U.S. Pat. 3,922,300 (Nov. 25, 1975), T. Onoda and co-workers (to Mitsubishi Chemical Industries Ltd.).
50. U.S. Pat. 4,010,197 (March 1, 1977), J. Toriya and K. Shiraga (to Mitsubishi Chemical Industries Ltd.).
51. U.S. Pat. 4,064,145 (Dec. 20, 1977), P. D. Taylor (to Celanese Corp.).
52. U.S. Pat. 4,356,125 (Oct. 26, 1982), N. A. de Munck and J. F. Scholten (to Stamicarbon B.V.).
53. Ger. Offen. 2,526,312 and 2,526,775 (both Dec. 30, 197), H. Moella and co-workers (to Henkel and Cie GmbH).
54. Jpn. Kokkai 75,142,537 (Nov. 17, 1975), Mizumoto and Kamatani (to Toyobo Co. Ltd.).
55. *Chem. Markt. Rep.*, 5 (May 15, 1995).
56. H. H. Chuah, "Polytrimethylene Terephthalate", *Encyclopedia of Polymer Science and Technology*, 3rd ed., Vol. III, John Wiley & Sons, Inc., New York, 2003, pp. 544–577.
57. U.S. Pat. 5,304,691 (April 19, 1994), J. P. Arhancet and L. H. Slaugh (to Shell Oil Co.).
58. U.S. Pat. 5,015,789 (May 14, 1991), D. Arntz and N. Wiegand (to ).
59. U.S. Pat. 6,342,464 (Jan. 29, 2002), J. P. Arhancet and co-workers (to Shell Oil Co.).
60. U.S. Pat. 6,191,321 (Feb. 20, 2001), T. C. Forschner, P. R. Wieder, L. H. Slaugh, and J. B. Powell (to Shell Oil Co.).
61. DE 3,734,764 A1 (May 1989), K. Tran-Dinh and F. F. Hill (to Hüls AG).
62. W.O. 9,928,480 (June 1999), R. V. Nair and co-workers (to E. I. du Pont de Nemours & Co and Genencor International Inc.).
63. U.S. Pat. 6,558,933 (May 6, 2003), T. E. Donald, W. M. Gregory, and O. V. Selifonova (to Genencor International Inc.).
64. U.S. Pat. 6,479,716 (Nov. 12, 2002), A. K. Hilaly and T. P. Binder (to Archer-Daniels Midland Co.).
65. *Chem. Eng. News* **81**(26), 33–34 (2003).
66. Tate and Lyle PLC, press release, May 26, 2004, see www.tateandlyle.com/PressReleases/PressRelease1261.asp.
67. R. Jakeways and co-workers, *J. Polym. Sci. Polym. Phys.* **13**, 799–813 (1975).
68. S. Poulin-Dandurand and co-workers, *Polymer* **20**, 419–426 (1979).
69. J. Desborough, I. H. Hall, and J. Z. Neisser, *Polymer* **20**, 545–552 (1979).
70. A. M. Brownstein, *CHEMTECH* **5** (Jan. 1995).
71. "New TPP challenges Nylon, PET, PBT " *Plastics Technol.* (July 1997).
72. S. R. Turner, R. W. Seymour, and T. W. Smith, "Cyclohexanedimethanol Polyesters", *Encyclopedia of Polymer Science and Technology*, 3rd ed., Vol. II, John Wiley & Sons, Inc., New York, 2003, pp. 127–134.

73. U.S. Pat. 2,901,466 (Aug. 25, 1959), C. J. Kibler, A. Bell, and J. G. Smith (to Eastman Kodak Co.).
74. J. Shimizu and co-workers, *J. Polym. Sci. Poly. Phys.* **21**(2), 275–284 (1983).
75. S. L. Sakellarides, "Polyethylene Naphthalate", *Encyclopedia of Polymer Science and Technology* 3rd ed., Vol. XI, John Wiley & Sons, Inc., New York, 2003, pp. 88–113.
76. Ref. 75 Table 3, p. 90.
77. D. C. Hoffman and T. J. Pecorini, *Polymer Preprints ACS Polymer Chem. Division*, **40**(1), 572 (1999).
78. A. S. Lindsey and H. Jeskey, *Chem. Rev.* **57**, 583 (1957).
79. PCT Intl. Appl. WO 86 02,924 (May 22, 1986), R. Ueno and co-workers (to Kabushiki Kaisha Ueno Seiyaku Oyo Kenkyujo). See *Chem. Abs.* **105**, 226054u (198).
80. Eur. Pat. Appl. EP 53,824 (June 16, 1982), R. Ueno and co-workers (to Kabushiki Kaisha Ueno Seiyaku Oyo Kenkyusho). See *Chem. Abs.* **97**, 182014r (1982).
81. U.S. Pat. 4,330,457 (May 18, 1982), A. J. East, L. F. Charbonneau, and G. W. Calundann (to Celanese Corp.).
82. Eur. Pat. 148,584 (Jan. 4, 1984), W. W. Kaeding (to Mobil Oil).
83. Eur. Pat. 271,623 (Dec. 19, 1986), S. Koskimies and T. Haimela (to Neste Oy).
84. Fr. Pat. 2,071,464 (Dec. 30, 1969), F. Bourdin and co-workers (to Rhone Poulenc).
85. Eur. Pat. 480,800 (Oct. 8, 1990), M. Costandini and M. Jouffret (to Rhone Poulenc).
86. U.S. Pat. 3,306,874 (Feb. 28, 1967), A. S. Hay (to General Electric Co.).
87. U.S. Pat. 4,205,187 (May 27, 1980), J. N. Cardenas and W. T. Reichle (to Union Carbide Corp.).
88. U.S. Pat. 4,524,217 (June 18, 1985), K. G. Davenport and C. B. Hilton (to Celanese Corp.).
89. W. L. Hergenrother and C. J. Nelson, *J. Poly. Sci. Poly. Chem. Ed.* **12**, 2905 (1974).
90. R. E. Wilfong, *J. Polym. Sci.* **54**, 388 (1961).
91. Fr. Pat. 1,169,659 (1959) (to ICI Ltd.).
92. Can. Pat. 573,301 (1959), W. K. Easley and co-workers (to Chemstrand Corp.).
93. H. Zimmerman and N. T. Kim, *Polym. Sci. Eng.* **20**(10), 680–683 (1980).
94. U.S. Pat. 4,501,878 (Feb. 26, 1985), L. J. Adams (to Eastman Kodak Co.).
95. U.S. Pat. 2,822,348 (1958), J. H. Haslam (to E. I. du Pont de Nemours & Co., Inc.).
96. U.S. Pat. 4,439,597 (March 27, 1984), H. K. Hall and A. B. Padias (to Celanese Corp.).
97. U.S. Pat. 4,824,930 (April 25, 1989), M. L. Doerr (to Celanese Fibers Inc.).
98. U.S. Pat. 4,511,708 (April 16, 1985), T. Kasuga and co-workers (to Polyplastics Company Ltd.).
99. U.S. Pat. 4,656,241 (April 7, 1987), H. Iida, K. Azuma, and M. Hayashi (to Toray Industries Inc.).
100. C. M. Fontana, *J. Polym. Sci., pt A-1*, **6**, 2343 (1968); Ref. 10 in this paper lists numerous U.S. Patents relating to antimony oxide as a polymerization catalyst.
101. U.S. Pat. 4,820,795 (April 11, 1989), S. Hirata and Y. Watanabe (to Toyo Seikan Kaisha).
102. U.S. Pat. 5,684,116 (Nov. 4, 1997), M. Martl and co-workers (to Akzo Nobel NV).
103. U.S. Pat. 5,789,528 (Aug. 4, 1998), M. Martl and co-workers (to Akzo Nobel NV).
104. E. A. Barringer and H. K. Bowen, *J. Am. Ceram. Soc.* **65**C, 199 (1982).
105. U.S. Pat. 5,552,513 (Sept. 3, 1996), K. K. Bhatia (to E. I. du Pont de Nemours & Co., Inc.).
106. U.S. Pat. 5,677,415 (Oct. 14, 1997), K. K. Bhatia (to E. I. du Pont de Nemours & Co., Inc.).
107. U.S. Pat. 5,856,423 (Jan. 5, 1999), K. K. Bhatia (to E. I. du Pont de Nemours & Co.).
108. U.S. Pat. 4,499,261 (Feb. 12, 1985), H. Heinze and co-workers (to Davy McKee AG).

109. U.S. Pat. 4,973,655 (Nov. 27, 1990), G. Pipper and co-workers (to BASF AG).
110. U.S. Pat. 5,064,935 (Nov. 12, 1991), R. Jackson, D. J. Lowe, and C. A. Stewart (to E. I. du Pont de Nemours & Co., Inc.).
111. Dr. U. K. Thiele; "The Polyester Resin Family", Proceedings of Global Conference on New Plastic Materials, Dusseldorf, October 23–24, 2001.
112. I. Goodman and B. F. Nesbitt, *J. Poly. Sci.* **48**, 423 (1960).
113. S. Shiono, *J. Poly. Sci. Poly. Chem. Ed.* **17**, 4123 (1979).
114. G. C. East and A. M. Girshab, *Polymer* **23**, 323 (1982).
115. U.S. Pat. 3,718,621 (Feb. 27, 1973), W. K. Wilson (to Goodyear Tire & Rubber Co.).
116. U.S. Pat. 3,816,377 (June 11, 1974), Y. Okuzumi (to Goodyear Tire & Rubber Co.).
117. U.S. Pat. 4,064,112 (Dec. 20, 1977), H. J. Rothe and co-workers (to Zimmer AG).
118. U.S. Pat. 4,161,578 (July 17, 1979), D. J. Herron (to Bepex Corp.).
119. L. H. Buxbaum, *Angew. Chem., Int. ed.* **7**, 182 (1968).
120. U.S. Pat. 4,137,278 (Jan. 30, 1979), A. L. Lemper and J. C. Rosenfeld (to Hooker Chemicals and Plastics Corp.).
121. I. Goodman, Ref. 1, p. 22.
122. S. Schauhoff, *Chem Fibers Int.*, Vol. **46**, (1996) p. 263.
123. H. Zimmerman and N. T. Kim, *Polym. Eng. Sci.* **20**(10), 680 (1980).
124. E. P. Goodings, *Soc. Chem. Ind. London, Chem. Eng. Group*, monograph 13, Society of Chemical Industry, London, 1961, p. 2112.
125. K. Tomita, *Polymer* **18**, 295 (1977).
126. A. von Hassell, *Plastics Technol.*, p. 70 (Jan. 1979).
127. U.S. Pat. 5,340,909 (Aug. 23, 1994), M. L. Doerr and J. J. Hammer (to Hoechst Celanese Corp.).
128. U.S. Pat. 6,277,947 (Aug. 21, 2001), D. R. Kelsey and co-workers (to Shell Oil Co.).
129. U.S. Pat. 5,798,433 (Aug. 25, 1998), W. Schmidt, U. Thiele, S. Schauhoff and D. Yu (to Zimmer AG and Degussa AG).
130. U.S. Pat. 6,281,325 (Aug. 28, 2001), J. V. Kurian and Y. Liang (to E. I. du Pont de Nemours & Co., Inc.).
131. U.S. Pat. 6,441,129 (Aug. 27, 2002), B. Duh and A. M. Corey (to Shell Oil Co.).
132. U.S. Pat. 6,610,819 (Aug. 26, 2003), B. Duh, R. L. Blackbourn, K. S. Kibler, and C. Z. Tse (to Shell Oil Co.).
133. Ref. 75, p. 98.
134. U.S. Pat. 4,963,644 (Oct. 16, 1990), B. Duh (to Goodyear Tire and Rubber Co.).
135. U.S. Pat. 3,549,593 (Dec. 22, 1970), T. Takekoshi (to General Electric Co.).
136. U.S. Pat. 4,161,470 (July 17, 1979), G. W. Calundann (to Celanese Corp.).
137. U.S. Pat. 4,431,770 (Feb. 14, 1984), A. J. East and G. W. Calundann (to Celanese Corp.).
138. U.S. Pat. 4,429,105 (Jan. 31, 1984), L. F. Charbonneau (to Celanese Co.).
139. U.S. Pat. 4,393,191 (July 12, 1983), A. J. East (to Celanese Corp.).
140. U.S. Pat. 4,093,595 (June 6, 1978), S. P. Elliot (to E. I. du Pont de Nemours & Co., Inc.).
141. U.S. Pat. 4,421,908 (Dec. 20, 1983), A. J. East (to Celanese Corp.).
142. U.S. Pat. 5,340,509 (Aug. 23, 1994), D. S. Chang, A. S. Rhee, R. K. Crossland, and J. O. Bühler-Vidal (to Shell Oil Co.).
143. *Plastics Technol.* **55** (April 1977); Ibid., 43 (Sept. 1977).
144. P. T. DeLassus and co-workers, *Mod. Plastics* 86 (Jan. 1983).
145. U.S. Pat. 3,733,309 (May 15, 1973), N. C. Wyeth and R. N. Roseveare.
146. U.S. Pat. 3,778,214 (Dec. 11, 1973), N. C. Wyeth and co-workers.
147. R. W. Tock and co-workers, *Adv. Polymer Technol.* **4**, 307 (1984).
148. Ball Industries Annual Report 2004.
149. E. A. Muccio, *Plastics Processing Technology*, Materials Information Society, 1994, Chapt. 5.

150. M. Cakmak, J. L. White, and J. E. Spruiell, *J. Appl. Poly. Sci.* **30**, 3679 (1985).
151. M. Cakmak, J. E. Spruiell, and J. L. White, *Polym. Eng. Sci.* **24**(18), 1390 (1984).
152. A. von Hassell, *Plastics Technol.* 74 (Jan. 1979).
153. A. von Hassell, *Plastics Technol.* 69 (Jan. 1979).
154. A. von Hassell, *Plastics Technol*. (Jan. 1979).
155. D. G. Callander, *Polym. Eng. Sci.* **25**(8), 453 (1985).
156. U.S. Pat. 4,578,437 (March 25, 1986), R. R. Light (to Eastman Kodak Co.).
157. P. A. Aspy and E. E. Denison, *Mod. Plastics* 74 (Aug. 1983).
158. D. G. Callander, Ref. 116, p. 456.
159. *Mod. Plastics*, 51 (July 2001).
160. L. M. Sherman, *Plastics Technol.* 55 (May 1995).
161. P. Reynolds, Testing the Power of PEN, Packaging World, July 1996.
162. S. Sacharow, *New Possibilities for Beer Packaging in PEN and LCP*, Paper Film and Foil Converters Sept. 1, 1996, available online at http://pffc-online.com.
163. Hyosung Chemicals data sheet, *PEN/coPEN*, available on line at www.hschem.biz.
164. K. R. Conrad and co-workers, *J. Food Sci*. **70**, E19 (2005).
165. U.S. Pat. 5,418,318 (May 23, 1995), A. S. Jones, D. E. Mills, and M. A. Winnick (to Eastman Chemical Co.).
166. L. M. Sherman, *Plastics Technol.* 57 (May 1995).
167. Kobe Steel Co. data sheet: “Applications for PEN” available online at www.kobelco.co.jp.
168. Anonymous; Res. Discl., 1987, 283, pp. 735–737.
169. Anonymous; Res. Discl., 1987, 283, pp. 705–710.
170. Anonymous; Res. Discl., 1987, 283, pp. 711–716.
171. Anonymous; Res. Discl., 1987, 283, pp. 699–703.
172. U.S. Pat. 6,656,577 (Dec. 2, 2003), D. J. Adelman, L. F. Charbonneau, and S. Ung (to E. I. du Pont de Nemours & Co., Inc.).
173. U.S. Pat. 6,359,070 (March 19, 2002), G. Khanarian, L. F. Charbonneau, and H. B. Witteler (to E. I. du Pont de Nemours & Co., Inc.).
174. U.S. Pat. 6,608,167 (Aug. 19, 2003), R. A. Hayes and C. J. Brandenberg (to E. I. du Pont de Nemours & Co., Inc.).
175. U.S. Pat. 6,818,730 (Nov. 16, 2004), C. J. Brandenberg and R. A. Hayes (to E. I. du Pont de Nemours & Co., Inc.).
176. Y. S. Hu and co-workers, *Macromolecules* **35**(19), 7326 (2002).
177. *Another Refillable PEN Bottle for Beer*, Packaging Magazine (May 31, 2001).
178. J. A. Grande, Plastics Technol. (Aug. 2005). (available online at www.plasticstechnology.com/articles) .
179. U.S. Pat. 4,550,043 (Oct. 29, 1985), M. H. Beck (to Continental Plastic Containers Inc.).
180. U.S. Pat. 4,954,376 (Sept. 4, 1990), S. M. Krishnakumar and co-workers (to Continental PET Technologies Inc.).
181. U.S. Pat. 5,077,111 (Dec. 31, 1991), W. N. Collette (to Continental PET Technologies Inc.).
182. *Plastics Technol*. (Jan. 2000).
183. Dow Chemical Company press release (Dec. 9, 2002).
184. P. Suppakul, J. Miltz, K. Sonneveld, and S. W. Bigger, *J. Food Sci.* **68**(2), 408 (2003).
185. *New PET Alloy Makes Monolayer Beer Bottle*: Asia-Pacific Magazine (Sept. 25, 2005) available online at www.ap-magazine.com.
186. A. K. Mitchell, *Mod. Plastics* **71**(12), B48 (1994).
187. S. Hoggard, *Plastic packaging in China* (2005), Pira International, available online at http://pira.atalink.co.uk/articles/packaging
188. *Plastics World* (Sept. 22, 2003).
189. R. Leaversuch, *Plastics Technol*. (May 2004).

190. *Plastics World* (April 25, 2005).
191. NAPCOR, PO Box 1327, Sonoma, CA 95476. See www.napcor.com.
192. G. R. Kenny and M. G. Roe (MSS Inc.); *Automatic Sorting of PEN Based Plastic Containers*, Novapak 97, obtainable online from www.magsep.com/PprNP97.htm
193. U.S. Pat. 4,074,032 (Feb. 14, 1978), H. Naarman and co-workers (to BASF AG.).
194. U.S. Pat. 4,143,221 (March 6, 1979), H. Naarman and co-workers (to BASF AG.).
195. U.S. Pat. 4,200,703 (April 29, 1980), K. Diebel and co-workers (to Chemische Werke Hüls AG.).
196. U.S. Pat. 4,360,455 (Nov. 23, 1982), G. Lindenschmidt and co-workers (to BASF AG.).
197. U.S. Pat. 4,352,909 (Oct. 5, 1982), H. J. Barda and S. L. Gray (to Ferro Corp.).
198. U.S. Pat. 4,879,353 (Nov. 7, 1989), D. C. Sanders and co-workers (to Great Lakes Chemical Corp.).
199. FAQs About PDBE Flame Retardants, Washington State Dept of Ecology, 2005, see www.ecy.wa.gov/programs.
200. *Mod Plastics* **71**(12), A40 (1994).
201. *Plastics News* (Feb. 23, 2004).
202. R. de P Daubeny and C. W. Bunn, *Proc. R. Soc.(London)* **A226**, 531 (1954).
203. S. Fakirov, E. W. Fischer, and G. F. Schmidt, *Makromol. Chem.* **176**, 2459 (1975).
204. E. Bornschegl and R. Bonart, *Coll. Polym. Sci.* **258**, 319 (1980).
205. Y. Kitano, Y. Kinoshita, and T. Ashida, *Polymer* **36**, 10 (1995).
206. M. Droscher, *Makromol. Chem.* **181**, 789 (1980).
207. H. W. Starkweather, P. Zoller, and G. A. Jones, *J. Poly. Sci. Poly. Phys. Ed.* **21**, 295 (1983).
208. J. Menczel and B. Wunderlich, *J. Poly. Sci., Poly. Lett. Ed.* **19**, 261 (1981).
209. K. H. Illers and H. Breuer, *J. Coll. Sci.* **18**, 1 (1963).
210. J. H. Dumbleton, T. Murayama, and J. P. Bell, *Kolloid Z. Z. Poly.* **228**, 54 (1968).
211. S. Berkowitz, *J. Appl. Poly. Sci.* **29**, 4353 (1984).
212. Hoechst Celanese Corporation (now Ticona): 1994 data Sheet for IMPET resins.
213. See Ref. 7.
214. M. Grossman, *Electronic Design* **37**(7), 19 (1989).
215. C. Lodge, *Plastics World* **47**(1), 48–50 (1989).
216. F. Liotine Jr., *J. Surf. Mount Tech. Assoc.* **17**(4) (2004).
217. C. A. Boye, *J. Poly. Sci.* **55**, 275 (1961).
218. A. B. Auerbach and J. W. Sell, *Poly. Sci. Eng.* **30**(17), 1041 (1990).
219. World Pat. 9,117,209 (Nov. 14, 1991), M. L. Cassell and co-workers (to Eastman Kodak Co.).
220. Eur. Pat. 273,149 (July 6, 1988), M. G. Minnick (to General Electric).
221. Jpn. Pat. 3,009,948 (June 6, 1989) (to Toray Industries ).
222. U.S. Pat. 5,124,435 (June 23, 1992), H. Mori and co-workers (to Mitsubishi Rayon Co. Ltd.).
223. U.S. Pat. 5,194,573 (March 16, 1993), W. Schmidt (to Zimmer AG).
224. U.S. Pat. 5,198,530 (March 30, 1993), M. Kyber and co-workers (to Zimmer AG).
225. R. M. Schulken, R. E. Boy, and R. H. Cox, *J. Poly. Sci., Part C* 17 (1964).
226. Eastman Publication PPD-115B, Nov. 1994.
227. M. C. Gabriele, *Plastics Technol.* 43 (May 1995).
228. Ger. Offen. 2,042,447 (April 15, 1971), D. D. Zimmerman and R. B. Isaacson; U.S. Appl. (Aug. 29, 1969) (to Celanese Corp.).
229. Ger. Offen. 2,533,358 (Feb. 26, 1976), F. M. Berardinelli; U.S. Appl. 496,607 (Aug. 12, 1974), (to Celanese Corp.).
230. E. Bornschegl and R. Bonart, *Coll. Poly. Sci.* **258**, 319 (1980).
231. I. H. Hall and M. G. Pass, *Polymer* **17**, 807 (1976).

232. R. Jakeways, I. M. Ward, and M. A. Wilding, *J. Polym. Sci., Poly Phys* **13**, 807 (1973).
233. K. H. Illers, *Coll. Polym Sci.* **258**(2), 117 (1980).
234. S. Z. D. Cheng, R. Pan, and B. Wunderlich, *Makromol. Chem.* **189**, 2443 (1988).
235. C. F. Pratt and S. Y. Hobbs, *Polymer* **17**, 12 (1976).
236. K. Tashiro and co-workers, *Macromolecules* **13**, 137 (1980).
237. W. F. H. Borman, *J. Appl. Poly. Sci.* **22**, 2119 (1978).
238. Ho Nan Sung, Hoechst Celanese Corporation, Summit N.J., private communication.
239. J. C. Gill, *Plastics Compounding*, 77–81 (Sept–Oct 1989).
240. L. M. Sherman, *Plastics Technol.* 32 (May 1994).
241. B. Miller, *Plastics World* 38 (Jan. 1995).
242. L. M. Sherman, *Plastics Technol* 27 (July 1995).
243. Rinkagaku Kogyo Co. Ltd: data sheet on red phosphorus as FR agent. see www.rinka.co.jp/english/products/retardant.
244. A. I. Belabanovitch and co-workers, *J. Fire Sci.* **20**(1), 71 (2002).
245. C. B. Bucknall, *Toughened Plastics*, publ. Applied Science, London (1977).
246. C. B. Bucknall and C. J. Page, *J. Mater. Sci.* 808 (1982).
247. D. J. Hourston, S. Lane, and H. X. Zhang, *Polymer* **32**(12), 2215 (1991).
248. Hoechst Celanese CELANEX Data Sheet CX-1A, Published 1992.
249. Ostrowski, de Kiewiet, *Mod. Plastics*, **71**(12), B67 (1994).
250. R. Leaversuch, *Plastics Technol*. (June 2004).
251. L. M. Sherman, and J. De Gaspari, *Plastics Technol.* 71 (Nov. 1995).
252. *DSM Ticona Joint Venture for PBT*, Netherlands Chemicals Technology, Nov. 15, 2002. see www.chemicals.technology.com/projects/dsm/.
253. J. De Gaspari, *Plastics Technol*. (July 1997).
254. B. Moss and D. L. Dorset, *J. Polym. Sci. Part B. Poly. Phys. Ed.*, **20**, 1782 (1982).
255. A. J. East, Polyester Fibers, *Synthetic Fibers*, J. E. McIntyre, ed., Woodhead Publications, Cambridge, U.K., 2004, Chapt. 3.
256. H. H. Chuah, D. Lin-Vein, and U. Soni, *Polymer* **42**, 7137 (2001).
257. H. L. Traub and co-workers, *Die Angew. Makromol. Chemie.* **230**, 179 (1995).
258. Z. Mencik, *Chem. Prim.* **17** part 2, 78 (1978).
259. N. R. Legge, G. Golden, and H. E. Schroeder, eds., *Thermoplastic Elastomers*, Hanser, 1987, pp. 163–196.
260. B. M. Walker and C. P. Rader, eds., *Handbook of Thermoplastic Elastomers*, 2nd ed., Van Nostrand Rheinhold Co., 1988, pp. 181–223.
261. Witsiepe, *ACS Adv. Chem. Ser.* **129**, 39 (1973).
262. Buck, Cella, Gladding, and Wolfe, *J. Poly. Sci.* **48**, 47 (1974).
263. Nelsen, Gromelski and Charles, *J. Elastomers Plastics* **15**, 10/83.
264. R. J. Cella, *J. Poly. Sci. Symp.* **42**, 727 (1973).
265. Hasketh, Van Bogart, and Cooper, *Poly. Eng. Sci.* **20**(3), 190 (Feb 1980).
266. Liliaonitkul, West, and Cooper, *J. Macromol. Sci.-Phys.*, B- **12**(4), 563 (1976).
267. Seymour, Overton, and Corley, *Macromolecules* **8**, 331 (1975).
268. Shen and co-workers, *J. Appl. Phys.* **45**, 4182 (1974).
269. West and co-workers, *ACS Polymer Preprints* **15**(2), 191 (1974).
270. Lilaonitkul and Cooper, *Rubber Chem. Technol.* **50**, 1 (1977).
271. Kaloglou, *J. Appl. Poly. Sci.* **21**, 543 (1977).
272. Miller and co-workers, *Macromolecules* **18**, 1727 (1985).
273. Apostolov and Fakirov, *J. Macromol. Sci. Phys.* 329 (1992).
274. Fakirov and co-workers, *Colloid Polym. Sci.* 811 (1993).
275. Riteflex Thermoplastic Polyester Elastomer; Hoechst Celanese Corp. Bulletin RF-4, 1993.
276. Riteflex Thermoplastic Polyester Elastomer Chemical Resistance Table Hoechst Celanese Corp. Material Monograph MRF-002.

277. HYTREL 10MS, DuPont Bulletin HYT-114.
278. U.S. Pat. 4,520,149 (May 28, 1985), M. D. Golder (to GAF Corp.).
279. Golder and Mulholland: Thermoplastic Elastomers 3, Rapra Technology Ltd. (1991). pp 20–23.
280. U.S. Pat. 4,405,749 (Sept. 20, 1983), S. B. Nelsen (to GAF Corp.).
281. U.S. Pat. 3,261,812 (July 19, 1966), A. Bell, C. J. Kibler, and J. G. Smith (to Eastman Kodak Co.).
282. Wolfe, *Rubber Chemistry and Technology*, Vol. **50**, 1977, p. 688.
283. G. K. Hoeschele, *Angew. Makromol. Chem.* **58–59**, 299 (1977).
284. U.S. Pat. 3,954,689 (May 4, 1976), G. K. Hoeschele (to E. I. du Pont de Nemours & Co.).
285. Wolfe, *ACS Advances in Chemistry Series*, Vol. **176**, 1979 p. 129.
286. Hudson, *Rubber World*, 23 (1991).
287. Blum, *1989 TPE Conference*, Orlando, Flor., March 1989.
288. Dolde, *1991, TPE Conference*, Orlando, Flor., February 1991.
289. Stahl, Paper No. 57. ACS Rubber Division, Cincinnati, Ohio, October 1988.
290. *Mod. Plastics*, **42** (March 1985).
291. Peffer, *1989, TPE Conference*, Orlando, Flor., March 1989.
292. Harding and Gerteisen; S.P.E. ANTEC, 1991, pp. 2409–2013.
293. Golder, *1990, TPE Conference*, Dearborn, Mich., March 1990.
294. U.S. Pat. 3,819,587 (June 25, 1974), S. L. Kwoleck (to E. I. DuPont de Nemours & Co., Inc.).
295. E. B. Priestley, P. J. Wojtowicz, and P. Sheng, *Introduction to Liquid Crystals*, Plenum Press, New York, 1975.
296. C. Carfagna, *Liquid Crystal Polymers*, Permagon, New York, 1994.
297. M. G. Dobb and J. E. McIntyre, *Adv. Polym. Sci.* **60–61**, 63 (1984).
298. G. W. Calundann and M. Jaffe, Anisotropic Polymers—Their Synthesis and Properties, *Proceedings of the Robert A Welch Conference on Chemical Research XXVI*, Houston Tex., November 1982, p. 247.
299. T. S. Chung, G. W. Calundann, and A. J. East, Liquid Crystal Polymers and Their Applications, *Handbook of Polymer Science and Technology*, N. P. Cheremisinoff, ed., Marcel Dekker, New York, 1989. pp. 625–675.
300. P. J. Flory, *Proc. R. Soc. London, Ser A* **234**, 60 (1956).
301. P. J. Flory, and G. Ronca, *Mol. Cryst. Liq. Cryst. Sci. Technol.* **54**, 289 (1979).
302. P. J. Flory, and M. Gordon, Liquid Crystal Polymers I, Vol. 59 of Advances in Polymer Science Series, Springer Verlag, New York, 1984, p. 1.
303. U.S. Pat. 4,067,852 (Jan. 10, 1978), G. W. Calundann (to Celanese Corp.).
304. U.S. Pat. 4,083,829 (April 11, 1978), G. W. Calundann, H. L. Davis, F. J. Gorman, and R. M. Mininni (to Celanese Corp.).
305. U.S. Pat. 4,902,772 (Feb. 20, 1990), N. Carter, B. P. Griffin, W. A. McDonald, and T. G. Ryan (to Imperial Chemical Industries plc).
306. A. Bunn, B. P. Griffin, W. A. McDonald, and D. G. Rance, *Polymer* **33**(14), 3066 (1992).
307. U.S. Pat. 3,637,597 (Jan. 25, 1972), S. G. Cottis, J. Economy, and B. E. Nowak.
308. U.S. Pat. 4,184,996 (Jan. 22, 1980), G. W. Calundann (to Celanese Corp.).
309. U.S. Pat. 4,219,461 (Aug. 26, 1980), G. W. Calundann (to Celanese Corp.).
310. U.S. Pat. 4,256,624 (March 17, 1981), G. W. Calundann (to Celanese Corp.).
311. U.S. Pat. 4,473,682 (Sept. 25, 1984), G. W. Calundann, L. F. Charbonneau, and B. C. Benicewicz (to Celanese Corp.).
312. U.S. Pat. 4,341,688 (July 27, 1982), L. F. Charbonneau, G. W. Calundann, and A. J. East (to Celanese Corp.).
313. U.S. Pat. 4,351,917 (Sept. 28, 1982), G. W. Calundann, L. F. Charbonneau, and A. J. East (to Celanese Corp.).

314. U.S. Pat. 4,351,918 (Sept. 28, 1982), L. F. Charbonneau, A. J. East, and G. W. Calundann (to Celanese Corp.).
315. U.S. Pat. 4,355,132 (Oct. 19, 1982), A. J. East, G. W. Calundann, and L. F. Charbonneau (to Celanese Corp.).
316. A. J. East, L. F. Charbonneau, and G. W. Calundann, *Mol. Cryst. Liq. Cryst., Sci Technol.* **157**, 615 (1988).
317. S. Kenig, *Polym. Eng. Sci.* **27**(12), 87 (1987).
318. U.S. Pat. 5,110,896 (May 5, 1992), M. G. Waggoner, and M. R. Samuels (to E. I. du Pont de Nemours & Co., Inc.).
319. U.S. Pat. 5,250,654 (Oct. 5, 1993), G. R. Alms, M. R. Samuels, and M. G. Waggoner (to E. I. du Pont de Nemours & Co., Inc.).
320. G. Kiss, *Polym. Eng. Sci.* **27**(6), 410 (1987).
321. *Plastics Technology, Manufacturing Handbook and Buyers' Guide*. Aug. 1995, pp. 490–492.
322. P. Zhuang, T. Kyu, and J. L. White, *Polym. Eng. Sci.* **28**(17) 1095.
323. F. N. Cogswell, *Recent Advances in Liquid Crystalline Polymers*, L. L. Chapoy, ed., Elsevier, New York, 1985, Chapt. 10.
324. D. W. Giles and M. M. Denn, *J. Rheol.* **38**, 617 (1994).
325. J. M. Dealy and K. Wissbrun, *Melt Rheology and Its Role in Plastics Processing*, Van Nostrand Reinhold, New York, 1990, pp. 424–440.
326. U.S. Pat. 4,468,364 (Aug. 28, 1984), Y. Ide (to Celanese Corp.).
327. C. E. McChesney, and J. R. Dole, *Mod. Plastics*, 112 (Jan. 1988).
328. F. C. Jaarsma, *S.P.E. ANTEC Preprints*, 406–407 (1990).
329. A. Kaslusky, *Mod. Plastics* B69 (Nov. 1994).
330. L. K. English, *Mater. Eng.* **106**(6), 29 (June 1989).
331. *Plastics News* (Oct. 10, 2005).
332. L. M. Sherman, *Plastics Technol*, 75 (May 1995).
333. M. Turano, Vectra global business Director, press statement, 2005.

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